SOLID STATE PHYSICS

for

CSIR-UGC-NET/JRF | GATE

Praveen Jaiswal

First Edition : July 2016

CAREER ENDEAVOUR PUBLICATIONS has taken due care in collecting the data and providing the solutions, before publishing this book. Inspite of this, if any inaccuracy or printing errors are there, CAREER ENDEAVOUR PUBLICATIONS owes no responsibility. CAREER ENDEAVOUR PUBLICATIONS will be grateful if you could point out any such error. Your suggestions will be highly appreciated.

© All right reserved by CAREER ENDEAVOUR PUBLICATIONS. No part of this book may be reproduced or utilized in any form without the written permission from the publisher.

CAREER ENDEAVOUR Publications

Regd. Office: 28-A/11, Jia Sarai, New Delhi-16, **Ph:** 011-26851008, 26861009

E: publications@careerendeavour.com, **W:** www.careerendeavour.com

CONTENTS

SOLID STATE PHYSICS

	Page No.
CHAPTER 1: Crystal Structure	01-37
CHAPTER 2: Reciprocal Lattice and X-ray Diffraction	38-62
CHAPTER 3: Crystal Bonding	63-71
CHAPTER 4: Lattice Vibrations	72-84
CHAPTER 5: Thermal Properties of Materials	85-106
CHAPTER 6: Free Electron Theory	107-124
CHAPTER 7: Band Theory of Solids	125-142
CHAPTER 8: Semiconductors	143-171
CHAPTER 9: Magnetic Properties of Materials	172-205
CHAPTER 10: Dielectrics	206-218
CHAPTER 11: Superconductivity	219-235
CHAPTER 12: Defects in Crystals	236-243
REFERENCE BOOKS	

Chapter 1

CRYSTAL STRUCTURE

Solids: The solids are the forms of matter in which atoms and molecules are strongly bound and maintain definite volume and shape unless changed by applying external forces.

Solid state physics: The solid state physics is the study of the physical properties of the atomic/molecular matter in the solid state. These physical properties include crystal structure, bonding, thermal, electrical and magnetic properties.

Classification of solids:

Solids are classified into two categories:
(i) crystalline solids
(ii) non-crystalline solids (amorphous)

Crystalline solids:

This crystalline solids are defined as an ordered periodic arrangement of atoms, molecules or ions.

Properties of crystalline solids:

(1) The internal arrangement of atoms, ions or molecules of crystalline solid is in a definite order.
(2) The crystalline solids have a sharp melting point.
(3) Below the temperature of crystallization, the crystalline materials are in a stable state. As the stable state is the state of minimum energy, materials acquire a state of minimum energy on crystallization.
(4) The orderly arrangement of atoms, ions and molecules in a crystal is extended over a large volume of the crystal, indicating a long range order by the atoms, ions and molecules.
(5) Crystalline solids are anisotropic. This implies that physical properties such as refractive index, conductivity, thermal properties such as expansion etc. are different in different directions. This is due to orderly arrangement of the constituents.
(6) Crystalline solids have uniform chemical composition throughout.

Examples: Diamond, Fe, Ag, Au, Salt, Sugar and Mica etc.

Non-crystalline solids:

Solids in which constituents (atoms, ions or molecules) are arranged in irregular or random manner are called amorphous solids or non-crystalline solids.

Properties of non-crystalline solids:

(1) The constituents are arranged in irregular manner.
(2) They do not have sharp melting point because the bonds between the atoms are not equally strong.
(3) They are isotropic in nature.
(4) Amorphous solids are regarded as supercooled liquids or pseudo solids.

Single crystalline solids:

When the periodicity of the pattern extends throughout a certain piece of solid material, it is called single crystalline solids. Example: Diamond. In a single crystal, same symmetry exists everywhere throughout the crystal.

Polycrystailine solids:

When a large number of small crystal sections (called grains) of various shapes and sizes are packed to one another separated by the interfaces (called grain boundaries) so that the periodicity is interrupted at the grain boundaries, though the structure may be more stable, the solid is called polycrystalline.

Crystallography: The science which deals with the structure of crystalline solids is called crystallography.

Crystal structure: The atomic arrangement in a crystal is called crystal structure.

In nature, most of the solids exit in crystalline form because crystalline form is more stable as compared to amorphous form of solids. The energy released during the formation of crystalline solids is more than the energy released during the formation of amorphous solids. As more released during the formation, the crystal will have less energy, thus the crystal will be more stable.

In order to describe crystal structure in detail, first we will discuss the following terms:

Crystal translation vectors, symmetry operations, crystal lattices and basis.

Crystal translation vectors:

A crystal is regular arrangement of atoms. We can imagine points in space about which these atoms are located. These points are called as lattice points. Thus an ideal crystal is a body composed of atoms arranged on a lattice defined by three fundamental translation vectors $\vec{a}, \vec{b}, \vec{c}$ such that the atomic arrangement looks the same in every respect when viewed from any point $\vec{r}$ as when viewed from the point $\vec{r}'$.

Thus, $\vec{r}' = \vec{r} + \vec{T} \Rightarrow \vec{r}' = \vec{r} + n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$ ... (i)

where n_1, n_2 and n_3 are arbitrary integers and $\vec{T}$ is called a lattice translation operation or crystal translation vector.

The crystal translation operation is defined as the displacement of a crystal parallel to itself by a crystal translation vector

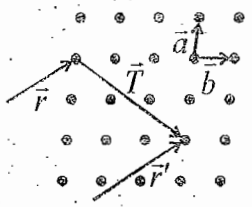
$$\vec{T} = n_1\vec{a} + n_2\vec{b} + n_3\vec{c} \quad \text{... (ii)}$$

In two dimensional lattice, the vector $\vec{T}$ connects any two points, as shown in figure and given by the following relation

$$\vec{T} = n_1\vec{a} + n_2\vec{b} \quad \text{... (iii)}$$

Lattice: A lattice is defined as parallel net like arrangement of points provided the environment about any point is identical with environment about any other point.

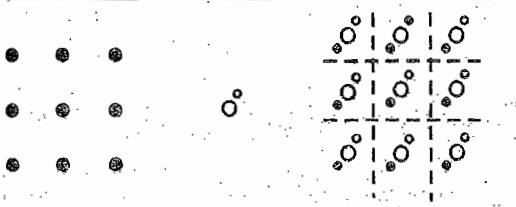
The figure shown below is an array of points in two dimensions, is called the plane lattice. If we extend this array of points in three dimensions then the array of points is called space lattice.



Basis: In order to get a crystal structure, an atom or group of atoms must be placed on each lattice point in regular manner. Such an atom or group of atoms is called the basis and acts as a building-block or unit for the crystal structure.

Mathematically, crystal structure can be expressed as

Space lattice + Basis = Crystal structure

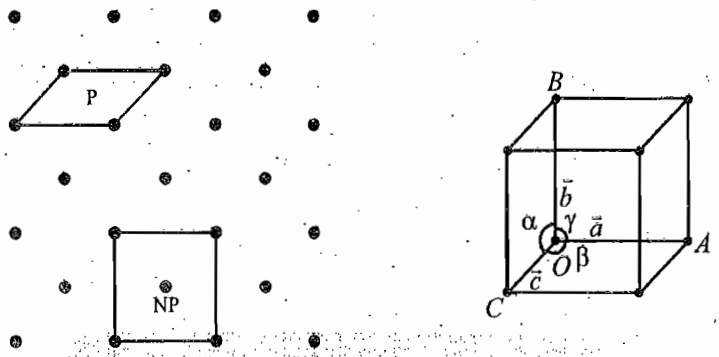


Lattice Basis Crystal structure

Unit cell: The parallelograms formed by the translation vectors are regarded as builiding blocks for constructing the complete lattice and are called as unit cells of the lattice. In three dimensions, this unit cell will be a parallelopiped. Therefore, a unit cell is defined as the smallest unit of lattice points which on repetition produces the complete lattice. There are two types of unit cells:

***(i)* Primitive unit cell (P):** The lattice points (atoms) belonging to primitive unit cell lie at its corners. The effective number of lattice points in a primitive unit cell is one.

***(ii)* Non-primitive unit cell (NP):** The lattice points (atoms) belonging to non-primitive cell lie at corners as well as other locations. The effective number of lattice points in a non-primitive unit cell is greater than one.



Wigner-Seitz cell:

A method for the construction of unit cell from the lattice points was given by Wigner-Seitz. The procedure of the construction is as follows:

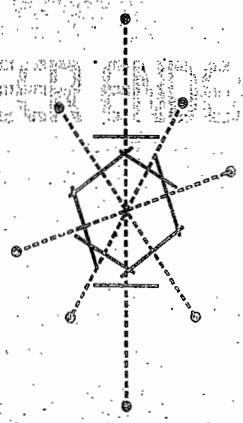
(1) connect a given lattice point to all the nearby lattice points

(2) draw normals at the midpoints of lines connecting the lattice points.

The smallest volume enclosed by the normals is the required primitive cell.

The cell constructed by this procedure is known as Wigner-Seitz cell.

In the figure, a two dimensional oblique lattice is constructed by this procedure and a hexagon is the result. Similarly, for a three dimensional BCC lattice, it is a truncated octahedron and for a FCC lattice, it is a rhombic dodecahedron, respectively.



Construction of Wigner-Seitz primitive cell

Crystal symmetry:

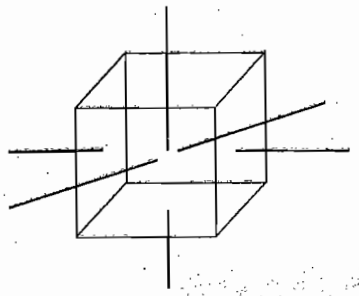
The operations that leaves the crystal and its environment invariant are called symmetry operations. There are four symmetry operations:

(i) Translational symmetry: A crystal translation is already defined in equations (ii) and (iii). Translation operations repeat the lattice infinite number of times along a given direction and leaves it unchanged.

(ii) Rotational symmetry: If after rotation of a lattice about an axis (or a point in two dimensional lattice) by some angle ϕ_n, the body appears as it did prior to rotation, the lattice is said to possess rotational symmetry. Axis of symmetry may thus be defined as a line such that the crystal assumes a congruent position (self-coincidence), for every rotation of $\left[\frac{360^\circ}{n}\right]$. The value of n decide the fold of the axis.

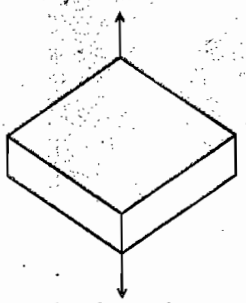
Only one, two, three, four and six-fold rotation axes of symmetry alone are possible in single crystal.

If a cube is rotated about a line perpendicular to one of its faces at its mid-point, it will turn into a congruent position every 90°, four times during a complete revolution. The normal is thus an axis of four fold symmetry, a tetrad axis.



(The three tetrad axis of a cube)

Let the cube be now rotated about a solid diagonal (body diagonal) through 120° to get congruence, and such a line, of which there are four, is therefore a triad axis.



(One of the triad axis of a cube)

Finally, a line joining the mid points of opposite parallel edges proves to be a diad axis.

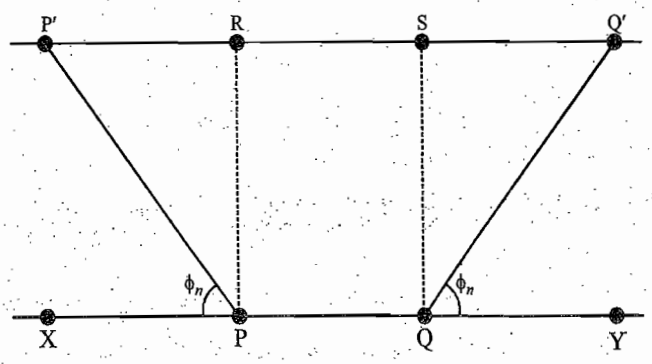
Total number of crystallographic symmetry elements of the cubic systems are thus,

$$1 + 3 + 6 + 3 + 4 + 6 = 23$$

Centre of symmetry	→	1
Straight planes	→	3
Diagonal planes	→	6
Tetrad axes	→	3
Triad axes	→	4
Diad axes	→	6

The fact that 5-fold rotation axis is not compatible with translation symmetry operation is proved as follows:

Consider a lattice row XPQY.



Let the lattice translation be a and the lattice have n-fold rotation axis of symmetry.

Let us rotate the vectors PX and QY through an angle $\phi_n = \left(\frac{360°}{n}\right)$ in clockwise and anticlockwise directions respectively. The tips of the vectors P′ and Q′ in the new position must be lattice points if the lattice possess n-fold rotation axis of symmetry.

As per definition, rotation operation must be the lattice invariant. Clearly P′Q′ must be parallel to PQ and must be equal to an integral multiple of the lattice translation a,

$P'Q' = ma$ where m is an integer.

Thus, $\cos\phi_n = \frac{P'R}{PP'}$ and $P'R = PP'\cos\phi_n = a\cos\phi_n$ and $SQ' = a\cos\phi_n \Rightarrow P'Q' = P'R + RS + SQ'$

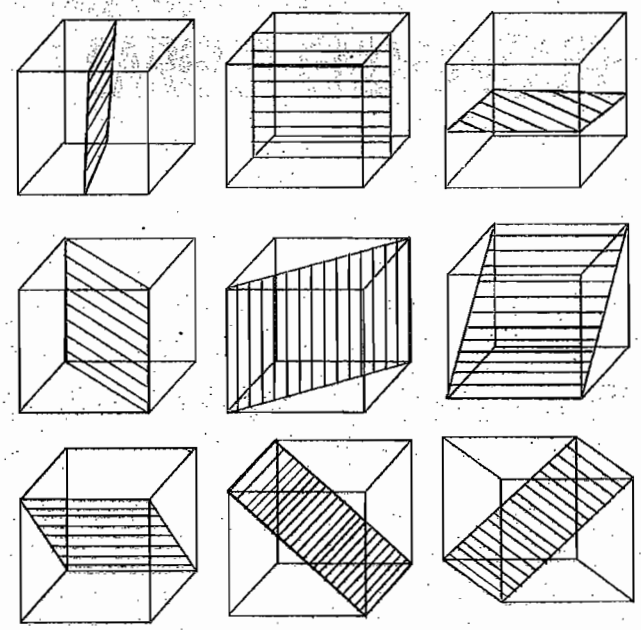
$$\Rightarrow P'Q' = 2a\cos\phi_n + a = ma \Rightarrow 1 + 2\cos\phi_n = m \Rightarrow 2\cos\phi_n = m - 1 = N \Rightarrow \cos\phi_n = \left(\frac{m-1}{2}\right) = \frac{N}{2}$$

N	$N/2$	$\cos\phi_n$	ϕ_n	N
−2	−1	−1	180°	2
−1	−1/2	−1/2	120°	3
0	0	0	90°	4
1	1/2	1/2	60°	6
2	1	1	360°	1

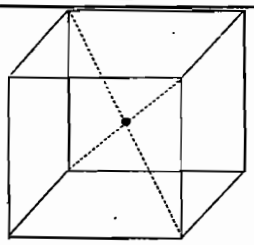
Hence, the permissible values of n are 2, 3, 4, 6, 1. Thus we conclude that 5-fold rotation is not permissible because it is not compatible with lattice translation symmetry.

Similarly, we can say that other rotations such as 7-fold rotation are also not permissible.

(iii) Reflection symmetry : A lattice possess reflection symmetry if there exist a plane (or a line into two dimensions) in the lattice which divides it into two identical halves which are mirror image of each other. Examples of this symmetry are shown in following figures.



(iv) Inversion symmetry : This is a point operation which is applicable to three-dimensional lattices only. This symmetry element implies that each point located at $\vec{r}$ relative to a lattice point has an identical point located at $-\vec{r}$ relative to the same lattice point.



Point group : Symmetry operations performed about a point or a line are called point group. There are total 10 point groups in two dimensional lattices and 32 point groups in three-dimensional lattices.

Space group : Symmetry operations performed by translation as well are called space group. There are total 17 space groups in two dimensional lattices and 230 space groups in three-dimensional lattices.

Types of lattices :

(i) Two-dimensional lattices : The four crystal systems of two dimensional lattices are given in following table.

Sr. No.	Crystal system	Bravais lattice	Conventional unit cell / Unit cell parameters
1.	Oblique	Oblique	Parallelogram $a \neq b, \gamma \neq 90°$
2.	Rectangular	(a) Rectangular primitive (b) Rectangular centered	Rectangle $a \neq b, \gamma = 90°$
3.	Square	Square	Square $a = b, \gamma = 90°$
4.	Hexagonal	Hexagonal	60° Rhombus $a = b, \gamma = 120°$

(ii) Three-dimensional lattices : There are 32 crystal structures based on geometrical considerations (i.e, symmetry and internal structure). But it is common practice to divide all crystal systems into seven groups or basic systems.

These seven basic crystal systems are shown in table with decreasing order of symmetry.

The crystallographic axes $\vec{a}, \vec{b}$ and $\vec{c}$ determines the size and shape of the unit cell. The angles α, β and γ represent the angles between the vectors $\vec{b}$ and $\vec{c}$, $\vec{c}$ and $\vec{a}$ and $\vec{a}$ and $\vec{b}$ respectively. These α, β, γ and a, b, c are collectively known as lattice parameters.

10 - 2D
32 - 3D
17 - 2D
230 - 3D

Sr. No.	Crystal system	Lattice parameters	Bravais lattice	Lattice symbol	Examples
1.	Cubic	$a=b=c$ $\alpha=\beta=\gamma=90°$	Simple Body-centered Face-centered	P I F	Cu, Ag, Fe, Na, NaCl, CsCl
2.	Tetragonal	$a=b\neq c$ $\alpha=\beta=\gamma=90°$	Simple Body-centered	P I	β-Sn, TiO_2
3.	Orthorhombic	$a\neq b\neq c$ $\alpha=\beta=\gamma=90°$	Simple Body-centered End-centered Face-centered	P I C F	Ga, Fe_3C (cementite)
4.	Rhombohedral or Trigonal	$a=b=c$ $\alpha=\beta=\gamma\neq 90°$	Simple	P	As, Sb, Bi
5.	Hexagonal	$a=b\neq c$ $\alpha=\beta=90°$, $\gamma=120°$	Simple	P	Mg, Zn, Cd, NiAs
6.	Monoclinic	$a\neq b\neq c$ $\alpha=\gamma=90°\neq\beta$	Simple End-centered	P C	$CaSO_4.2H_2O$ (gypsum)
7.	Triclinic	$a\neq b\neq c$ $\alpha\neq\beta\neq\gamma\neq 90°$	Simple	P	$K_2Cr_2O_7$

Miller indices:

Crystal lattice may be regarded as made up of an aggregate of a set of parallel equidistant planes passing through the lattice points. These equidistant planes are called as lattice planes. The scheme to represent the orientation of lattice planes was given by Miller (a British crystallographer). He has given some indices to represent a set of planes. The indices of planes are known as Miller indices. For a general set of planes, Miller indices are written as $(h\,k\,l)$.

The steps involved in calculation of Miller indices is given below.

(i) Determine the coordinates of the intercepts made by the plane along the three crystallographic axes (x, y, z axes).

x	y	z	
pa	qb	rc	
$2a$	$3b$	c	(suppose)

$\Rightarrow p=2, q=3$ and $r=1$

(ii) Express the intercepts as multiples of the unit cell dimensions or lattice parameter along the axes i.e.,

$\frac{2a}{a}$	$\frac{3b}{b}$	$\frac{c}{c}$
2	3	1

(iii) Determine the reciprocals of these numbers $\frac{1}{2}\quad\frac{1}{3}\quad\frac{1}{1}$.

(iv) Reduce these reciprocals to the smallest set of integral numbers and enclose them in bracket with comma.

$$6\times\frac{1}{2} \qquad 6\times\frac{1}{3} \qquad 6\times 1$$

$$(3 \qquad 2 \qquad 6)$$

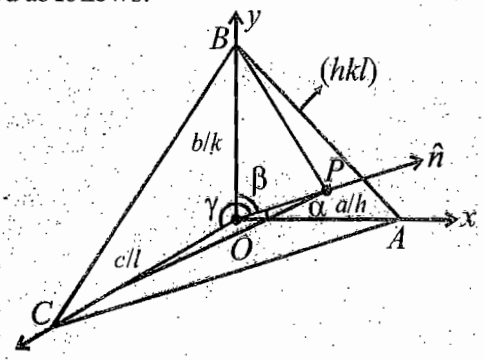
Thus the Miller indices of the planes is (3 2 6).

Thus, Miller indices may be defined as the reciprocals of the intercepts made by plane on the cyrstallographic axes when reduces to smallest numbers.

$$h:k:l=\frac{a}{\text{OA}}:\frac{b}{\text{OB}}:\frac{c}{\text{OC}}$$

where, a, b and c are lattice parameters along x-, y- and z-axes respectively. OA, OB and OC are intercepts on a-, b- and c-axis respectively.

Relation between interplanar spacing and lattice parameters : If the plane have ($h\,k\,l$) miller indices then its intercepts can be calculated as follows:



$$h:k:l=\frac{a}{OA}:\frac{b}{OB}:\frac{c}{OC}$$

Therefore, intercepts $OA=\frac{a}{h}$, $OB=\frac{b}{k}$ and $OC=\frac{c}{l}$.

Now, if we draw a perpendicular (normal) from origin (O) to the plane ($h\,k\,l$) at P. Then OP will be the interplanar spacing (d) between two planes which are parallel to ($h\,k\,l$) and also passes through O.

$$\therefore\quad d=OP=\frac{a}{h}\cos\alpha=\frac{b}{k}\cos\beta=\frac{c}{l}\cos\gamma$$

where α, β and γ represent the angles between the normal and the axes $\vec{a}$, $\vec{b}$ and $\vec{c}$ respectively and $\cos\alpha$, $\cos\beta$ and $\cos\gamma$ represent the direction cosines of the normal to the plane ($h\,k\,l$).

Cosine rule: $\cos^2\alpha+\cos^2\beta+\cos^2\gamma=1$

$$\Rightarrow\left(\frac{hd}{a}\right)^2+\left(\frac{kd}{b}\right)^2+\left(\frac{ld}{c}\right)^2=1$$

$$\Rightarrow\ d^2\left(\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}\right)=1$$

$$\Rightarrow\ d=\left(\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}\right)^{-1/2}\quad\text{or}\quad d=\frac{1}{\sqrt{\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}}}$$

There is another way to show this relation. Let $\hat{n}$ be the unit vector in the direction $\overrightarrow{OP}$.

$$\therefore \quad d = \hat{n}\cdot\frac{\vec{a}}{h} = \hat{n}\cdot\frac{\vec{b}}{k} = \hat{n}\cdot\frac{\vec{c}}{l}$$

The equation of plane, $f(x, y, z) = \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c}$

For a surface $f(x, y, z) =$ constant, ∇f represents the vector normal to it.

$$\therefore \quad \hat{n} = \frac{\nabla f}{|\nabla f|} = \frac{\left(\frac{h}{a}\right)\hat{i} + \left(\frac{k}{b}\right)\hat{j} + \left(\frac{l}{c}\right)\hat{k}}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$$

$$\therefore \quad d = \hat{n}\cdot\frac{\vec{a}}{h} = \left\{\frac{\left(\frac{h}{a}\right)\hat{i} + \left(\frac{k}{b}\right)\hat{j} + \left(\frac{l}{c}\right)\hat{k}}{\sqrt{\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)}}\right\}\cdot\frac{\vec{a}}{h}$$

$$\Rightarrow \quad d = \frac{1}{\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)^{1/2}}$$

(where $a \neq b \neq c$, therefore this relation corresponds to orthorhombic structure)

For cubic structure, $a = b = c$, $d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$

For tetragonal structure, $a = b \neq c$, $d = \frac{1}{\sqrt{\left(\frac{h^2 + k^2}{a^2}\right) + \frac{l^2}{c^2}}}$.

Different crystal structures:

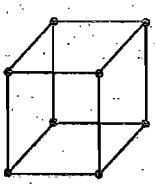
Cubic crystal structures:

(i) Simple cubic crystal structure (SC):

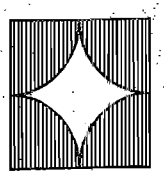
In a simple cubic structure there is one lattice point (atom) at each of the eight corners (shares 1/8 part of the atom) of the cubic unit cell. This is primitive unit cell structure of cubic crystal system. Properties of simple cubic strucutre are given below.

(a) Number of nearest neighbours:

If we take a lattice point at one corner as the origin, it is observed that this atom is surrounded by six equidistant nearest neighbours at coordinates $(+a, 0, 0)$, $(-a, 0, 0)$, $(0, +a, 0)$, $(0, -a, 0)$, $(0, 0, a)$ and $(0, 0, -a)$. The coordination number is defined as the number of nearest neighbours to a given atom in the crystal lattice. Thus, for simple cubic structure, the coordination number is six. The distance of these nearest neighbours is a.



Unit cell of SC structure

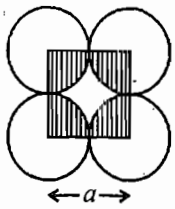


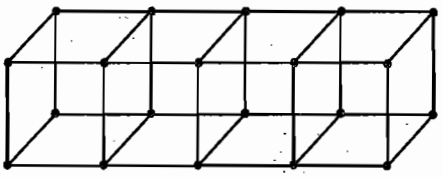
Plane view of SC structure

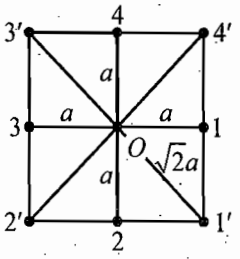
In this structure, each corner atom is shared by eight unit cell.

(b) Number of second nearest neighbours: There are 12 second nearest neighbours at distance $\sqrt{2}a$.

(c) Atomic radius: From this figure, $a = 2r \Rightarrow r = \frac{a}{2}$.







(d) Number of atoms per unit cell: The number of effective lattice points (atoms) per unit cell is given by

$$n_{eff} = n_i + \frac{n_f}{2} + \frac{n_c}{8}$$

where, n_i is the number of lattice points (atoms) completely inside the cell and n_f and n_c represent the lattice points occupying face center and corner positions of the cell, respectively.

For SC structure, $n_i = 0, n_f = 0$ and $n_c = 8$, $n_{eff} = 1 \times 0 + \frac{1}{2} \times 0 + \frac{1}{8} \times 8 = 1$.

(e) Atomic packing fraction: The packing of atoms in a unit cell of the crystal structure of a material is represented by atomic packing fraction (APF). The APF is defined as the ratio of volume occupied by the atoms in a unit cell to that of the volume of the unit cell.

$$\text{APF} = \left(\frac{\text{volume of the atoms per unit cell}}{\text{volume of the unit cell}}\right) = \left(\frac{n_{eff} \times \text{volume of each atom}}{\text{volume of unit cell}}\right)$$

For simple cubic structure, $n_{eff} = 1$

$$\therefore \quad \text{APF} = \frac{1 \times \frac{4}{3}\pi r^3}{a^3} = \frac{1 \times \frac{4}{3}\pi\left(\frac{a}{2}\right)^3}{a^3} = \frac{4}{3}\pi \times \frac{1}{8} = \frac{\pi}{6} = 0.52.$$

$$\therefore \quad \text{APF}\% = 52\%.$$

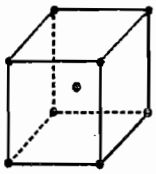
(f) Type of packing: Simple cubic structure is a loose-packed structure.

(g) Example : Only Polonium exhibits this type of structure at room temperature.

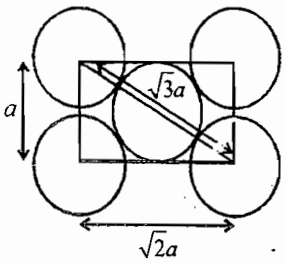
(ii) Body centered cubic structure (BCC):

In the BCC structure, there is one lattice point (atom) at each corners (shares 1/8th part of the atom) of the cubic unit cell and one lattice point (atom) exit at the body center. This is non-primitive unit cell structure of cubic crystal system.

The corner atoms do not touch each other, but each corner atom touches the body centered atom along the body diagonal.



Conventional unit cell of BCC structure



Plane view of BCC structure

(a) Number of nearest neighbours: If we take, the body centered lattice point (atom) of cell as origin then all the corner atoms at coordinates $\left(+\frac{a}{2},+\frac{a}{2},+\frac{a}{2}\right),\left(+\frac{a}{2},+\frac{a}{2},-\frac{a}{2}\right),\left(+\frac{a}{2},-\frac{a}{2},+\frac{a}{2}\right),\left(+\frac{a}{2},-\frac{a}{2},-\frac{a}{2}\right),$ $\left(-\frac{a}{2},+\frac{a}{2},+\frac{a}{2}\right),\left(-\frac{a}{2},+\frac{a}{2},-\frac{a}{2}\right),\left(-\frac{a}{2},-\frac{a}{2},+\frac{a}{2}\right)$ and $\left(-\frac{a}{2},-\frac{a}{2},-\frac{a}{2}\right)$ will be nearest neighbours to the body centered atom. Since, there are 8 corners therefore, number of nearest neighbours (i.e. coordination number) will be 8. The distance of these nearest neighbours from reference lattice point is $\frac{\sqrt{3}a}{2}$.

(b) Number of second nearest neighbours: There are 6 second nearest neighbours at distance a in BCC structures.

(c) Atomic radius: From above figure, $4r=\sqrt{3}a \Rightarrow r=\frac{\sqrt{3}a}{4}$.

(d) Number of atoms per unit cell: The number of effective lattice points (atoms) per unit cell is given by

$$n_{eff}=n_i+\frac{n_f}{2}+\frac{n_c}{8}$$

where, n_i is the number of lattice points (atoms) completely inside the cell and n_f and n_c represent the lattice points occupying face center and corner positions of the cell, respectively.

For BCC structure, $n_i=1, n_f=0$, and $n_c=8$, $n_{eff}=1\times1+\frac{1}{2}\times0+\frac{1}{8}\times8=2$.

(e) Atomic packing fraction: $\text{APF}=\left[\frac{n_{eff}\times\text{volume of each atom}}{\text{volume of unit cell}}\right]$

For BCC structure, $n_{eff}=2$

$$\therefore\ \text{APF}=\frac{2\times\frac{4}{3}\pi r^3}{a^3}=\frac{2\times\frac{4}{3}\pi\left(\frac{a\sqrt{3}}{4}\right)^3}{a^3}=\frac{\sqrt{3}\pi}{8}=0.68$$

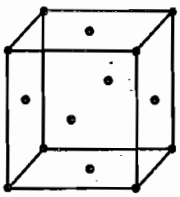
$$\therefore\ \text{APF}\%=68\%$$

(f) Type of packing: Body centered cubic structure is a loose-packed structure.

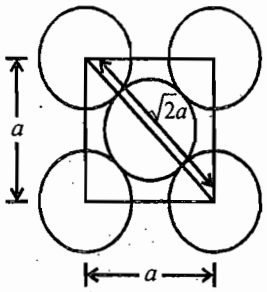
(g) Examples: Li, Na, K, Mo etc.

(iii) Face-centered cubic structure (FCC):

In FCC structure, one atom lies at each corner of the cube in addition to one atom at the center of each face. This is also a non-primitive unit cell structure of cubic crystal system.



Conventional unit cell of FCC structure



Plane view of FCC structure

(a) Number of nearest neighbours : If we take, one of the face centered lattice point (atom) of unit cell as origin then all the 12 corner atoms at coordinates $\left(+\frac{a}{2},+\frac{a}{2},0\right),\left(+\frac{a}{2},-\frac{a}{2},0\right),\left(-\frac{a}{2},-\frac{a}{2},0\right),\left(-\frac{a}{2},+\frac{a}{2},0\right),$ $\left(+\frac{a}{2},0,+\frac{a}{2}\right),\left(+\frac{a}{2},0,-\frac{a}{2}\right),\left(-\frac{a}{2},0,-\frac{a}{2}\right),\left(-\frac{a}{2},0,+\frac{a}{2}\right),\left(0,+\frac{a}{2},+\frac{a}{2}\right),\left(0,+\frac{a}{2},-\frac{a}{2}\right),\left(0,-\frac{a}{2},-\frac{a}{2}\right)$ and $\left(0,-\frac{a}{2},+\frac{a}{2}\right)$ will be nearest neighbours to this face centered atom. These atoms will lie at corners of the three faces in x, y and z-axes passing through the reference atom. Hence, total number of nearest neighbours (i.e. coordination number) will be 12. The distance of these nearest neighbours from reference lattice point is $\frac{\sqrt{2}a}{2}$ or $\frac{a}{\sqrt{2}}$.

(b) Number of second nearest neighbours : There are 6 second nearest neighbours at distance a in FCC structures.

(c) Atomic radius: From above figure, $4r=\sqrt{2}a \Rightarrow r=\frac{\sqrt{2}a}{4}=\frac{a}{2\sqrt{2}}$.

(d) Number of atoms per unit cell: The number of effective lattice points (atoms) per unit cell is given by

$$n_{eff}=n_i+\frac{n_f}{2}+\frac{n_c}{8}$$

where, n_i is the number of lattice points (atoms) completely inside the cell and n_f and n_c represent the lattice points occupying face center and corner positions of the cell, respectively.

For FCC structure, $n_i=0$, $n_f=6$ and $n_c=8$, $n_{eff}=1\times0+\frac{1}{2}\times6+\frac{1}{8}\times8=3+1=4$.

(e) Atomic packing fraction : $\text{APF}=\left[\frac{n_{eff}\times\text{volume of each atom}}{\text{volume of unit cell}}\right]$

For FCC structure, $n_{eff}=4$

$$\therefore\ \text{APF}=\frac{4\times\frac{4}{3}\pi r^3}{a^3}=\frac{4\times\frac{4}{3}\pi\left(\frac{\sqrt{2}a}{4}\right)^3}{a^3}=\frac{\sqrt{2}\pi}{6}=0.74$$

$$\therefore\ \text{APF}\%=74\%$$

(f) Type of packing: Face-centered cubic strucutre is a close-packed structure.

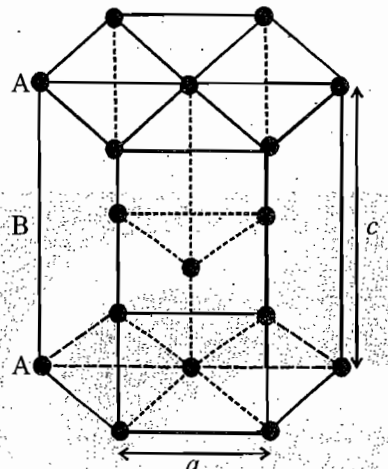
(g) Examples: Cu, Au, Ag, Al etc.

Hexagonal close packed structure (HCP):

The specific hexagonal structure formed by Magnesium is shown in figure. The unit cell contains one atom at each corner, one atom at the centre of each hexagonal faces and three more atoms within the body of the cell.

(a) Number of nearest neighbours: Each atom touches six atoms in its plane, three atoms in the layer below its plane, and three atoms in the layer above. Hence the coordination number of this structure is 12. Further the atoms touch each other along the edge of the hexagon. Thus, $a = 2r$.

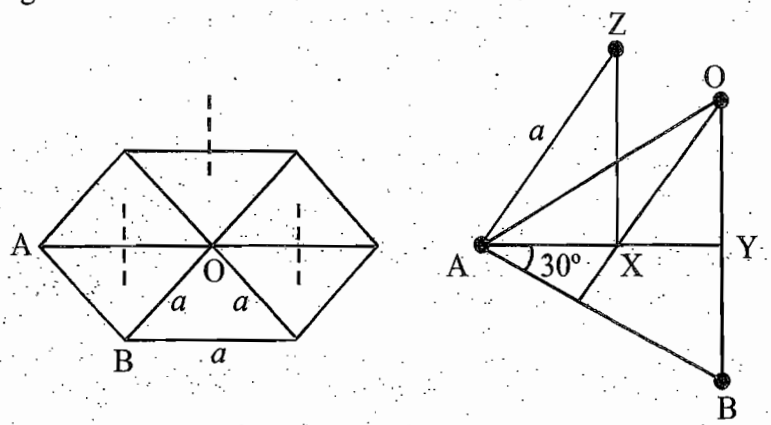
The top layer contains seven atoms. Each corner atom is shared by 6 surrounding hexagon cells and the centre atom is shared by two adjacent cells. The three atoms within the body of the cell are fully contributing to the cell.



Conventional unit cell of HCP structure

(b) Number of atoms per unit cell: In this structure, there are 12 atoms at 12 corners of the hexagonal unit cell, two atoms at the center of top and bottom hexagons and three atoms inside the unit cell. Thus, the effective number of atoms in a unit cell is $\frac{1}{6} \times 12 + \frac{1}{2} \times 2 + 1 \times 3 = 6$.

(c) Calculation of (c/a) ratio for an ideal HCP structure : Let c be the height of the unit cell and a equilateral triangles at the top or base of the hexagonal cell. These three atoms just rest on the three atoms at the corners of the triangles.



Plane view of HCP structure

In the triangle ABY, $\cos 30° = \frac{AY}{AB}$

$$AY = a\cos 30^\circ = \frac{a\sqrt{3}}{2} \text{ and } (AZ)^2 = (AX)^2 + (ZX)^2 \quad \ldots (i)$$

In triangle AXZ, $AX = \frac{2}{3}AY = \frac{2}{3}\left(\frac{a\sqrt{3}}{2}\right) = \frac{a}{\sqrt{3}}$

Substituting AZ, AX and ZX in equation (i), we get

$$a^2 = \frac{a^2}{3} + \frac{c^2}{4} \Rightarrow \frac{c^2}{4} = a^2 - \frac{a^2}{3} = \frac{2a^2}{3} \Rightarrow \frac{c^2}{a^2} = \frac{8}{3} \Rightarrow \frac{c}{a} = \sqrt{\left(\frac{8}{3}\right)}$$

(d) Volume of the unit cell :

Area of the base = six times the area of the triangle AOB

Area of the triangle, $AOB = \frac{1}{2} \times BO \times AY = \frac{1}{2} \times a \times \frac{\sqrt{3}a}{2} = \frac{\sqrt{3}a^2}{4}$

Thus, area of the base $= 6 \times \frac{\sqrt{3}a^2}{4} = \frac{3}{2}\sqrt{3}a^2$

Volume of the cell $= \frac{3}{2}\sqrt{3}a^2c$.

(e) Calculation of APF for HCP structure :

Coordination number, $N = 12$; Lattice constant, $a = 2r$

Nearest neighbour distance, $2r = a$; Number of atoms per unit cell, $n = 6$

Volume of one atom in a unit cell $= \frac{4}{3}\pi r^3 = \frac{4}{3}\pi\left(\frac{a}{2}\right)^3 = \frac{\pi a^3}{6}$

Volume of unit cell $= \frac{3}{2}\sqrt{3}a^2c$ with $c/a = \left(\frac{8}{3}\right)^{1/2}$

Atomic packing factor, $APF = \left[\frac{n_{eff} \times \text{volume of each atom}}{\text{volume of unit cell}}\right]$

$$\therefore \quad APF = \frac{6 \times (\pi a^3/6)}{\frac{3}{2}\sqrt{3}\,a^2c} = \frac{2\pi}{3\sqrt{3}}\left(\frac{a}{c}\right) = \frac{2\pi}{3\sqrt{3}}\left(\frac{3}{8}\right)^{1/2} = \frac{\sqrt{2}\pi}{6} = \frac{\pi}{3\sqrt{2}} = 0.74$$

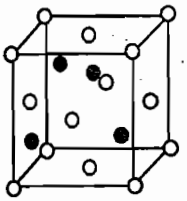
$\therefore$ APF% = 74%

(f) Type of packing: The packing fraction of FCC and HCP are 74% and hence they are known as close-packed structures.

(g) Examples: Magnesium, zinc, cadmium etc.

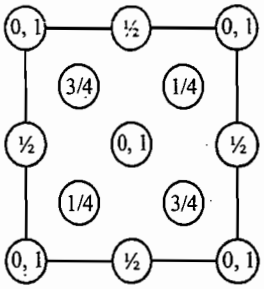
Diamond Cubic Structure:

The diamond lattice can be considered to be formed by two interpenetrating FCC lattices along the body diagonal by one-fourth of cube edge. One sublattice has its origin at the point (0, 0, 0) and the other at a point quarter of the way along the body diagonal [i.e. at the point (a/4, a/4, a/4)]. The basic diamond lattice and the atomic positions in the cubic cell of diamond lattice are shown in figure. The fractions denote height about the base in units of cube edge. The point at 0 and 1/2 are on the FCC lattice, those at 1/4 and 3/4 are on a similar lattice displaced along the body diagonal by 1/4th of the cube edge.



○ : Carbon atom occupying DC structure
● : Carbon atom occupying tetrahedral sites

Unit cell of DC structure



Plane view of atomic positions in DC unit cell. Numbers in the circles indicate fractional heights of the carbon atoms.

This is not a Bravais lattice.

(a) Number of nearest neighbours (coordination numbers): Each carbon atom has four nearest neighbours at distance $\sqrt{3}a/4$. Therefore, the co-ordination number is 4.

(b) Number of second nearest neighbours: There are 12 second nearest neighbours at distance $a/\sqrt{2}$.

(c) Atomic radius: From the plane view of DC structure it is clear that $8r = \sqrt{3}a \Rightarrow r = \frac{\sqrt{3}a}{8}$.

(d) Number of atoms per unit cell: $n_{eff} = \frac{1}{8} \times 8 + \frac{1}{2} \times 6 + 4 = 8$

(e) Atomic packing fraction : $\text{APF} = \left[\frac{n_{eff} \times \text{volume of each atom}}{\text{volume of unit cell}}\right]$

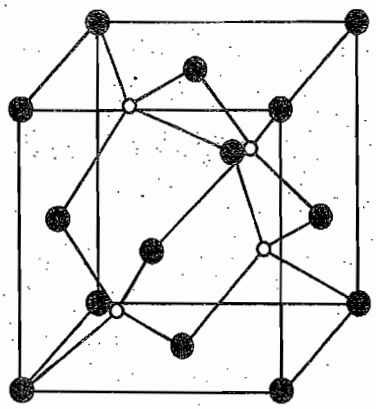
$$\therefore \text{APF} = \frac{8 \times \frac{4}{3}\pi r^3}{a^3} = \frac{8 \times \frac{4}{3}\pi \left(\frac{\sqrt{3}a}{8}\right)^3}{a^3} = 8 \times \frac{4}{3}\pi \times \frac{3\sqrt{3}}{8 \times 8 \times 8} = \frac{\sqrt{3}\pi}{16} = 0.34$$

$\therefore$ APF % = 34%.

(f) Type of packing: Diamond cubic is a loose-packed structure.

(g) Example : Carbon, silicon, germanium etc.

Zinc Blende structure (ZnS) : Zinc blende structure is almost identical to the diamond structure except that the two interpenetrating FCC sublattices are of different atoms and displaced from each other by one-quarter of the body diagonal.



○ Zn-atom occupying tetrahedral site
● S-atoms occupying FCC position

The unit cell of Zinc blende (ZnS) structure

The cubic zinc sulphide structure results when Zn-atoms are placed on one FCC lattice and S-atoms on the other FCC lattice as shown in figure. The conventional cell of this structure is a cube. There are four molecules per conventional cell. For each atom, there are four equally distant atoms of opposite kind arranged at a regular tetrahedron.

The ZnS is not an atomic structure. It is a molecular structure. For this structure, nearest neighbour distance $= r_{Zn} + r_S$. In a unit cell of ZnS, there will be 4 Zn-atoms and 4 S-atoms.

(a) Atomic radius: $a = \frac{4}{\sqrt{3}}(r_{Zn} + r_S)$

(b) Atomic packing fraction: $\text{APF} = \left[\frac{n_{eff} \times \text{volume of each atom}}{\text{volume of unit cell}}\right]$

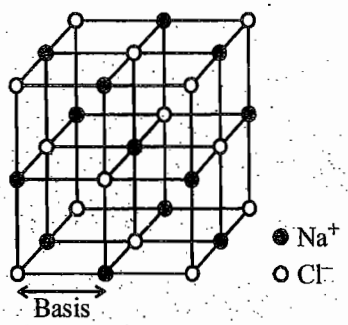
$$\therefore \quad \text{APF} = \frac{4\times\left(\frac{4}{3}\pi r_{Zn}^3 + \frac{4}{3}\pi r_S^3\right)}{a^3} = \frac{4\times\frac{4}{3}\pi r_{Zn}^3 + 4\times\frac{4}{3}\pi r_S^3}{\left(\frac{4}{\sqrt{3}}\right)^3 (r_{Zn}+r_S)^3} = \left\{\frac{r_S^3\left(1+\frac{r_{Zn}^3}{r_S^3}\right)}{r_S^3\left(1+\frac{r_{Zn}}{r_S}\right)^3}\right\}\times\left(\frac{\sqrt{3}\pi}{4}\right)$$

$$= \frac{\sqrt{3}}{4}\pi\left\{\frac{1+\left(\frac{r_{Zn}}{r_S}\right)^3}{\left(1+\frac{r_{Zn}}{r_S}\right)^3}\right\}$$

(c) Examples: The compounds which have cubic zinc sulphide structure are CuCl, ZnS, InSb and CdS.

Sodium chloride structure:

In sodium chloride, sodium loses its outer electron and acquires an excess of positive charge while the chlorine atom accepts one electron from sodium and becomes a negative ion. Now, due to the electrostatic forces between the excess charges, the two ions attract each other. Further, due to the strong forces of repulsion as their outer electron shells come into close proximity, the two ions cannot approach each other to within less than certain distance. When attraction and repulsion balance, equilibrium is obtained. The Bravais lattice is a face centred cube, with a basis of one Na^+ ion and one Cl^- ion separated by one-half the body diagonal of the unit cell. There are four molecules of NaCl in a unit cell, with ions in the positions.



Unit cell of sodium chloride structure

$$Na^+ : \left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right), \left(0,0,\frac{1}{2}\right), \left(0,\frac{1}{2},0\right), \left(\frac{1}{2},0,0\right)$$

$$Cl^- : (0,0,0), \left(\frac{1}{2},\frac{1}{2},0\right), \left(\frac{1}{2},0,\frac{1}{2}\right), \left(0,\frac{1}{2},\frac{1}{2}\right)$$

(a) Number of nearest neighbours (coordination number): Nearest neighbours of Na^+ ions are 6 Cl^- ions. Similarly nearest neighbours of Cl^- ions ions are 6 Na^+ ions. Therefore, the co-ordination number of NaCl structure is 6. The distance of nearest neighbour is $r_{Na} + r_{Cl} = \frac{a}{2}$.

(b) Second nearest neighbours: There are 12 second nearest neighbours for each Na^+ and Cl^- ions at $\frac{a}{\sqrt{2}}$ distance.

(c) Number of atoms per unit cell: Total number of Cl^- ions $= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$

$$\text{Total number of } Na^+ \text{ ions} = \frac{1}{4} \times 12 + 1 = 3 + 1 = 4$$

This is also a molecular crystal structure.

(d) Atomic packing fraction: $\text{APF} = \left[\frac{n_{eff} \times \text{volume of each atom}}{\text{volume of unit cell}}\right]$

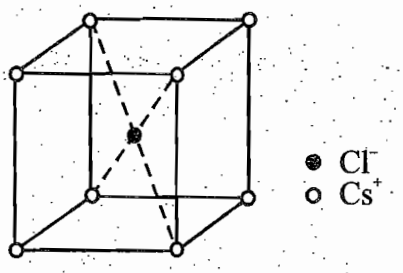
$$\therefore \quad \text{APF} = \frac{4 \times \left(\frac{4}{3}\pi r_{Na}^3 + \frac{4}{3}\pi r_{Cl}^3\right)}{a^3} = \frac{4 \times \frac{4}{3}\pi r_{Na}^3 + 4 \times \frac{4}{3}\pi r_{Cl}^3}{8\left(r_{Na} + r_{Cl}\right)^3} = \frac{2\pi}{3} \frac{\left(r_{Na}^3 + r_{Cl}^3\right)}{\left(r_{Na} + r_{Cl}\right)^3} = \frac{2}{3}\pi \left\{\frac{1 + \left(\frac{r_{Cl}}{r_{Na}}\right)^3}{\left(1 + \frac{r_{Cl}}{r_{Na}}\right)^3}\right\}$$

(e) Examples : Representative crystals having NaCl structure are KCl, KBr, MgO, AgBr, etc.

Cesium chloride structure:

The space lattice of cesium chloride (CsCl) structure is simple cubic. The basis has one Cs^+ ion at (0, 0, 0) and one Cl^- ion at $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$. Each ion is at the centre of a cube of ions of the opposite kind; the coordination number is thus eight. Obviously, the lattice points of CsCl are two interpenetrating simple cubic lattices, the corner of one sublattice is the body centre of the other. One sublattice is occupied by Cs^+ ions and the other by Cl^- ions.

The unit cell of CsCl structure is shown in the figure shown below.



The unit cell of Cesium chloride structure

(a) Number of nearest neighbours: There are 8 nearest neighbour lattice points (atoms) at distance $\left(\frac{\sqrt{3}a}{2} = r_{Cs} + r_{Cl}\right)$ in CsCl structure. For Cs^+ ion nearest neighbours are 8 Cl^- ions. Similarly, for Cl^- ion nearest neighbours are 8 Cs^+ ions.

(b) Second nearest neighbours: There are 6 second nearest neighbours at distance a.

(c) Number of atoms per unit cell : There are two ions (one Cs^+ and another Cl^-) per unit cell i.e. one molecule of CsCl.

(d) Atomic packing fraction:

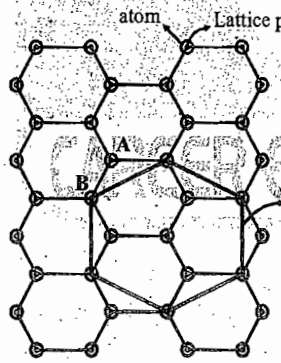
$$APF = \left[\frac{n_{eff} \times \text{volume of each atom}}{\text{volume of unit cell}}\right] = \frac{1 \cdot \frac{4}{3}\pi\left(r_{Cs}^3 + r_{Cl}^3\right)}{a^3} = \frac{\frac{4}{3}\pi\left(r_{Cs}^3 + r_{Cl}^3\right)}{\left(\frac{2}{\sqrt{3}}\left(r_{Cs} + r_{Cl}\right)\right)^3}$$

$$= \frac{\sqrt{3}}{2}\pi\frac{\left(r_{Cs}^3 + r_{Cl}^3\right)}{\left(r_{Cs} + r_{Cl}\right)^3} = \frac{\sqrt{3}}{2}\pi\frac{\left(1 + \frac{r_{Cl}^3}{r_{Cs}^3}\right)}{\left(1 + \frac{r_{Cl}}{r_{Cs}}\right)^3}$$

(e) Examples: CsCl, RbCl, LiHg etc. Simple Cubic.

Graphene:

Graphite structure is made up of graphene layers graphene has honeycomb structure i.e., carbon atoms are arranged in the honeycomb structure. In 2-dimensions one C-atom is shared by 3 nearby C-atoms. This is the graphite structure in 2-dimensional. In 3-dimensions, one C-atom is shared by 6 nearby C-atoms.



Graphite structure is layered structure but graphene is a single layered structure (single layer of carbon atom).

Graphite is conductor because there is one electron free per carbonatom.

If consider lattice point on each atom position then it will not form a basis because surroundings of A and B are different.

Only A-A atoms or B-B atoms can form basis as they have same surrounding.

So either connect nearby A-A atoms or B-B atoms. This hexagon (red) is the unit cell of graphene.

(1) This unit cell is non-primitive.

(2) **Number of atoms per unit cell:**

$$\text{Corners atoms} = \frac{1}{3} \times 6 = 2$$

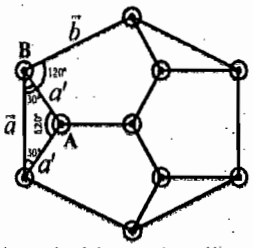
$$\text{Inside atoms} = 1 \times 4 = 4$$

Therefore, total numbers of atoms/unit cell = 6

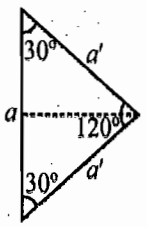
The side of unit cell is lattice parameter a. All the sides of this structure will be same.

Let lattice parameters is a. Thus, $|\vec{a}| = |\vec{b}|, \gamma = 120°$

(3) **Nearest neighbour distance:** $2r = a' = \frac{a}{\sqrt{3}}$.



Primitive unit cell



From figure, $\cos 30° = \frac{a/2}{a'}$

$\Rightarrow \frac{\sqrt{3}}{2} = \frac{a}{2a'}$

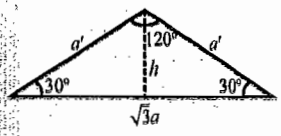
$\Rightarrow a' = \frac{a}{\sqrt{3}}$

(4) Number of nearest neighbours = 3.
In 2-dimensions, there will be close packing if number of nearest neighbours are 6 but here 3 so packing will be loose.

(5) Second nearest neighbour distance = a

(6) Number of second nearest neighbours = 6

(7) Area of triangle $= \frac{1}{2} \times \sqrt{3}a \times \frac{a}{2} = \frac{\sqrt{3}a^2}{4}$



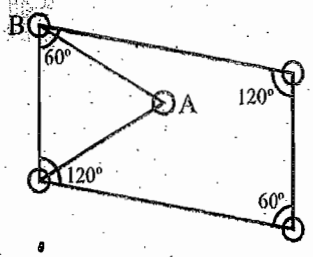
$h^2 = a^2 - \frac{3}{4}a^2 = \frac{a^2}{4} \Rightarrow h = \frac{a}{2}$

Area of 2 triangle $= \frac{\sqrt{3}a^2}{2}$

Area of unit cell $= \sqrt{3}a^2 + \frac{\sqrt{3}a^2}{2} = \sqrt{3}\left(1 + \frac{1}{2}\right)a^2 = \frac{3\sqrt{3}a^2}{2}$

(8) Area of primitive unit cell $= \frac{1}{3} \times$ area of unit cell $= \frac{1}{3}\left(\frac{3\sqrt{3}}{2}\right)a^2 = \frac{\sqrt{3}a^2}{2}$

(9) Number of atoms per primitive unit cell = 1 + 1 = 2
Therefore, 2 atoms of graphene inside the primitive cell.
Thus, graphene has 2 atom basis (i.e., one atom of A type and one of B-type)



(10) **Number of atoms per unit area:**

Number of atoms per unit area $= \frac{6}{\left(\frac{3\sqrt{3}a^2}{2}\right)} = \frac{4}{\sqrt{3}a^2}$

Number of atoms $= \left(\frac{1}{6} + \frac{1}{3} + \frac{1}{3} + \frac{1}{6}\right) = 1$

(11) **Atomic radius :** $r = \frac{a}{2\sqrt{3}}$

(12) **Type of packing:** loose

(13) **Example :** Graphene

(14) **Atomic Packing Fraction (APF):**

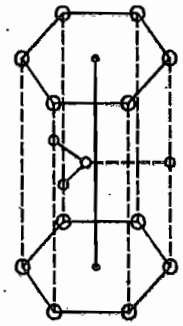
$$\text{APF} = \frac{\text{area of the atoms in unit cell}}{\text{area of unit cell}} = \frac{6 \times \pi r^2}{\frac{3\sqrt{3}a^2}{2}} = \frac{12\pi r^2}{3\sqrt{3} \times 4 \times 3 \times r^2} = \frac{\pi}{3\sqrt{3}} = 0.604.$$

$\{a = 2\sqrt{3}r$ and area of the atoms $= \pi r^2\}$

Therefore, APF = 60 %

Graphite : Graphite is a form of carbon and crystalises in simple hexagonal structure. It contains 4 atoms per primitive unit cell.

Number of atom per unit cell: Number of atoms per unit cell $= \frac{1}{6} \times 12 + \frac{1}{3} \times 3 = 3 + 1 = 4$



Height of the unit cell = 4.8 times the nearest neighbours distance

Nearest neighbour distance implies $2r = a$, a is lattice parameter

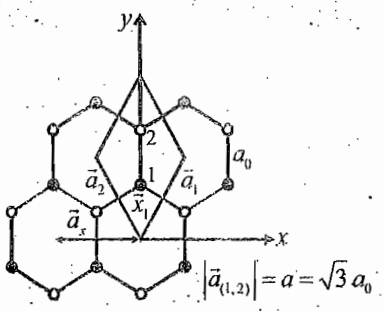
Number of nearest neighbour = 3.

One C-atom can make covalent bond with 3 nearby atoms, C-atoms of one layer can not make bond with C-atom of second layer. That's why graphite sheets slides on each other. Therefore, graphite is soft because layer do not have bonding.

Since, semiconductor are not conducting at $T = 0$ K and metals are conducting at $T = 0$ K
Graphite is a semi-metal.

Wigner Seitz unit cell (Hexagon in this case):

- a_1 and a_2 are the primitive vectors of the graphene unit cell.
- Area of the unit cell will be $\sqrt{3}\ a^2/2$ where a is the lattice parameter.
- a_0 shown in the figure is nearest-neighbour distance but not lattice parameter .
- Bravais lattice of graphene is either hexagonal or triangular with basis as shown previously.



$\vec{a}_1 = a_0\sqrt{3}(1/2, \sqrt{3}/2)$

$\vec{a}_2 = a_0\sqrt{3}(-1/2, \sqrt{3}/2)$

Relation between lattice constant and density:

Let the lattice parameter of the unit cell is a. Therefore, the volume of the unit cell is a^3.

If ρ be the density of the unit cell then the mass of each unit cell = $a^3\rho$ ...(1)

If M is the molecular weight and N is the Avogadro number.

$\therefore$ Mass of each molecule = $\frac{M}{N}$

As if n is the number of molecules per unit cell, then the mass in each unit cell = $n \times \frac{M}{N}$ ... (2)

From equations (1) and (2), we get

$$a^3\rho = n\frac{M}{N} \quad \Rightarrow \quad a = \left(\frac{nM}{N\rho}\right)^{1/3}$$

Atomic density: The number of atoms per unit area of a lattice plane is called as atomic density.

Atomic density (ρ) = $\frac{nd}{V}$, where V = volume of unit cell and n is the number of atoms in it and d is the interplanar spacing.

$\therefore$ $\rho = \frac{nd}{abc}$

If $n = 1 \Rightarrow \rho = \frac{d}{abc}$

Planes in different crystals:

1. **Simple cubic structure :**

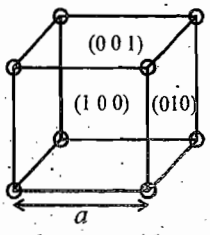
Plane analysis in semiconductor

First consider (1 0 0) plane

In planes (0 1 0), (0 0 1), (1 0 0), the properties are same.

Number of atoms on (1 0 0) type plane = $\frac{1}{4} \times 4 = 1$

Area of plane = a^2



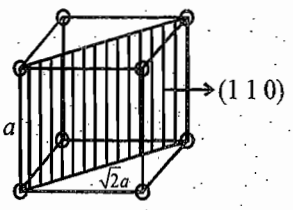
For a plane, consider atoms as disc (in two dimension)

Therefore, atomic density = number of atoms per unit area = $\frac{1}{a^2}$

(1 1 0) plane :

Number of atoms = $\frac{1}{4} \times 4 = 1$.

Area = $\sqrt{2}a^2$ (Since, shape is rectangular)



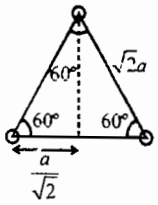
Therefore, atomic density = $\frac{1}{\sqrt{2}a^2}$

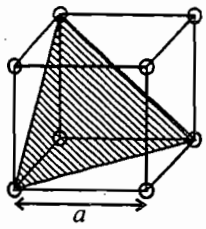
(1 1 1) plane :

Number of atoms $= \frac{1}{6} \times 3 = \frac{1}{2}$

Area $= \frac{1}{2} \times$ base $\times$ height (Since, shape is triangular)

$= \frac{1}{2}\left(\sqrt{2}a\right)\sqrt{\frac{3}{2}}a = \frac{\sqrt{3}a^2}{2}$





$h^2 = 2a^2 - \frac{a^2}{2}$

$h^2 = \frac{3a^2}{2} \Rightarrow h = \sqrt{\frac{3}{2}}a$

Therefore, atomic density $= \frac{1}{\sqrt{3}a^2}$

Example: Which plane in simple cubic is closed pack plane ?

Soln. Plane having (1 0 0) largest atomic density will be closed packed plane.

Example: Which direction is closest pack in simple cubic lattice ?

Soln. In one dimensions, atom is considered as a line
In 2 dimensions, atom is considered as a disc
In three dimensions, atom is considered as a sphere
Directions having largest line density will be closest pack

Simple cubic structure:

Among planes (1 0 0), (1 1 0), (1 1 1), $(1\bar{1}0)$, line density of (1 0 0) is largest.
Therefore, (1 0 0) is the closest pack direction.

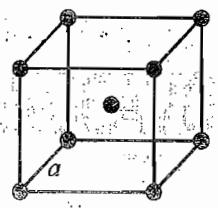
[In distance a there are 1 atom $\left(\frac{1}{2}+\frac{1}{2}=1\right)$]. (i.e., line density $= 1/a$)

Body Centred Cubic Structure (BCC):

(1 0 0) plane :

Number of atoms = 1 (no new atom on faces)

Area $= a^2$



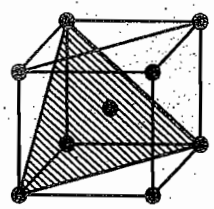
Plannar density $= \frac{1}{a^2}$

Line density $= \frac{1}{a}$

(1 1 0) plane :

Number of atoms = 2

Area $= \sqrt{2}a^2$



Planner density $= \frac{\sqrt{2}}{a^2}$

Line density $= \frac{1}{\sqrt{2}}a$

(1 1 1) plane :

Number of atoms $= \frac{1}{2}$

(Body centered atom will not contribute to (1 1 1) plane)

$$\text{Area} = \frac{\sqrt{3}a^2}{2}$$

$$\text{Planner density} = \frac{1}{\sqrt{3}a^2}$$

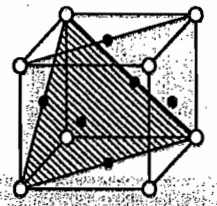
$$\text{Line density} = \frac{2}{\sqrt{3}a}$$

For BCC closest pack plane is (1 1 0).

Face Centred Cubic Structure (FCC):

(1 0 0) plane :

$$\text{Number of atoms} = \frac{1}{4} \times \overset{\text{corners}}{4} + \overset{\text{face}}{1} = 2$$



Area = a^2

$$\text{Planner density} = \frac{2}{a^2}$$

$$\text{Line density} = \frac{1}{a}$$

(1 1 0) plane :

$$\text{Number of atoms} = \frac{1}{4} \times 4 + \frac{1}{2} \times 2 = 2$$

Area = $\sqrt{2}a^2$

$$\text{Planner density} = \frac{\sqrt{2}}{a^2}$$

$$\text{Line density} = \frac{\sqrt{2}}{a}$$

(1 1 1) plane :

$$\text{Number of atoms} = \frac{1}{6} \times 3 + \frac{1}{2} \times 3 = 2$$

Area = $\frac{\sqrt{3}}{2}a^2$

$$\text{Planner density} = \frac{4}{\sqrt{3}a^2}$$

$$\text{Line density} = \frac{1}{\sqrt{3}a}$$

For FCC closest pack plane is (1 1 1).

SOLVED PROBLEMS

1. **Calculate the lattice constant** of NaCl Crystal. The density of NaCl is 2189 kg/m^3 and Avogadro number (N_A) is 6.02×10^{26} /kg-mol.

Soln. Molecular weight of NaCl = 58.5 kg / kg-mol (or gm/gm-mol)

For FCC structure, $n_{eff} = 4$

For FCC lattice, $a = \left(\dfrac{nM}{N_A\rho}\right)^{1/3}$

$$\Rightarrow \quad a = \left[\frac{4\times58.5}{6.02\times10^{26}\times2189}\right]^{1/3} = \left(177\times10^{-30}\right)^{1/3} = 5.61\times10^{-10}\ \text{m} = 5.61\ \text{Å}$$

Hence, the lattice parameter of NaCl crystal is 5.61 Å.

2. Find the ratio of intercepts on the three axes by $(1\bar{3}2)$ planes in simple cubic lattice.

Soln. Let p, q, r are the intercepts on the x, y and z-axis respectively.

Then, $p:q:r = \dfrac{a}{h}:\dfrac{b}{k}:\dfrac{c}{l}$

$$\Rightarrow \quad p:q:r = \frac{a}{1}:\frac{a}{-3}:\frac{a}{2} = 6:-2:3$$

Hence, the ratio of intercepts on the three axes is 6:-2:3.

3. In a tetragonal lattice $a = b = 2.5$ Å, $c = 1.8$ Å. Deduce the lattice spacing between (1 1 1) planes.

Soln. Lattice spacing between (111) planes:

$$d_{hkl} = \frac{1}{\sqrt{\left(\dfrac{h^2}{a^2}+\dfrac{k^2}{b^2}+\dfrac{l^2}{c^2}\right)}} = \frac{1}{\sqrt{\left(\dfrac{1^2}{1.8^2}+\dfrac{1^2}{1.8^2}+\dfrac{1^2}{2.5^2}\right)}} = 1.26\ \text{Å}$$

4. For a simple cubic crystal find (i) the ratio of intercepts on the three axes by (1 2 3) plane, (ii) the ratio of the spacings of (1 1 0) and (1 1 1) plane and (iii) the ratio of nearest neighbour distance to the next nearest neighbour distance.

Soln. (i) $p:q:r = \dfrac{a}{h}:\dfrac{b}{k}:\dfrac{c}{l}$

$$p:q:r = \frac{a}{1}:\frac{a}{2}:\frac{a}{3} = 6:3:2$$

(ii) $d_{hkl} = \dfrac{a}{\sqrt{h^2+k^2+l^2}}$

For (110) plane, $d_{110} = a/\sqrt{2}$

For (111) plane, $d_{111} = a/\sqrt{3}$

$$\therefore \quad \frac{d_{110}}{d_{111}} = \sqrt{3}:\sqrt{2}$$

(iii) In a simple cubic lattice, distance between nearest neighbours is a and distance between next nearest neighbours is $\sqrt{2}a$.

$$\text{Their ratio} = \frac{a}{\sqrt{2}a} = 1:\sqrt{2}.$$

5. Calculate the density of (1 0 0) planes in a simple cubic (P) lattice; given $a = 2.5$ Å.

Soln. Density, $\rho = \frac{d}{a^3}$

Here, $d_{100} = a$

$$\rho = \frac{a}{a^3} = \frac{1}{a^2} = \frac{1}{\left(2.5\times10^{-10}\,m\right)^2} = 1.6\times10^{19} \text{ per m}^2$$

6. Compare the densities of lattice points in (1 1 1) and (1 1 0) planes in an simple cubic lattice.

Soln. Density, $\rho = \frac{d}{abc} = \frac{d}{a^3} \Rightarrow \frac{\rho_{111}}{\rho_{110}} = \frac{d_{111}}{d_{110}} \Rightarrow \frac{\rho_{111}}{\rho_{110}} = \frac{a/\sqrt{3}}{a/\sqrt{2}} = \frac{\sqrt{2}}{\sqrt{3}}$.

7. Sodium transform from body-centered cubic to hexagonal close-packed crystal structure at 23 K without change of density in the cubic face $a = 4.23$ Å and in hexagonal close-packed face $\frac{c}{a} = 1.63$. Find lattice constant in hexagonal close-packed face.

Soln. Let volume of BCC cell $= a_1^3$ and volume of HCP cell $= \frac{3\sqrt{3}}{2}a_2^2c$.

$\because$ mass = volume × density

$\Rightarrow$ volume of BCC = volume of HCP

$$\Rightarrow \frac{3\sqrt{3}}{2}a_2^2c = a_1^3,\ \frac{c}{a_2} = 1.63$$

$$\Rightarrow \frac{3\sqrt{3}}{2}\times a_2^3(1.63) = a_1^3,\ c = 1.63\,a_2 \Rightarrow \frac{3\sqrt{3}}{2}\times a_2^3(1.63) = (4.23)^3$$

$$\Rightarrow a_2 = \left(\frac{(4.23)^3\times2}{3\times1.732\times1.63}\right)^{1/3} \Rightarrow a_2 = 2.6144 \text{ Å}$$

Hence, lattice constant in HCP face = 2.6144 Å.

CAREER ENDEAVOUR

8. Find the Miller indices for planes in each of the following sets which intercepts $\vec{a}, \vec{b}$ and $\vec{c}$ at

(i) $3a, 3b, 2c$; (ii) $a, 2b, \infty$; (iii) $a, b/2, c$ (iv) $3a, 2b, 2c$

Soln. (i) Set of intercepts are $3a, 3b, 2c$.

Reciprocal of numbers representing the intercepts are $\frac{1}{3}, \frac{1}{3}, \frac{1}{2}$.

Smallest three integers having the same ratio are 2, 2, 3.
Therefore, Miller indices are (2 2 3).

(ii) Set of intercepts are $a, 2b, \infty$.

Reciprocals of numbers are $1, \frac{1}{2}, 0$.

Smallest three integers having the same ratio are 2, 1, 0.
Therefore, Miller indices are (2 1 0).

(iii) Set of intercepts are $a, \frac{b}{2}, c$.

Reciprocal of numbers are 1, 2, 1.

Therefore, Miller indices are (1 2 1).

(iv) Sets of intercepts are $3a, 2b, 2c$.

Reciprocals of numbers representing the intercepts are $\frac{1}{3}, \frac{1}{2}, \frac{1}{2}$.

Smallest three integers having the same ratio are 2, 3, 3.

Therefore, Miller indices are (2 3 3).

9. Calculate the separation between lattice planes in a simple cubic (SC), face-centred cubic (FCC) and body-centred cubic (BCC) lattice.

Soln. **Simple cubic lattice :** A simple cubic lattice has (1 0 0), (1 1 0) and (1 1 1) planes. The (1 0 0) planes cut the x-axis and are parallel to y and z-axis.

$$\Rightarrow \quad d_{100} = \frac{a}{\left(1^2 + 0 + 0\right)^{1/2}} = a$$

The (1 1 0) planes cut obliquely across x and y axis but are parallel to z-axis.

$$\Rightarrow \quad d_{110} = \frac{a}{\left(1^2 + 1^2 + 0\right)^{1/2}} = \frac{a}{\sqrt{2}}$$

The (1 1 1) planes cut the x, y and z-axis.

$$\therefore \quad d_{111} = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{a}{\sqrt{3}}.$$

Face centred cubic lattice : In FCC lattice there is one unit situated at each corner and one unit at the center of each of the six faces. Thus, an additional (1 0 0) plane arises half way between the (1 0 0) planes. These additional planes pass through the centre of the front and back face. As the distance between (1 0 0) planes of a simple cubic lattice is a, the distance between (1 0 0) planes of the FCC lattice is $\frac{a}{2}$.

$$\Rightarrow \quad d_{100} = \frac{1}{2}a$$

CAREER ENDEAVOUR

Similarly, there arises an additional set of (1 1 0) planes parallel to the first set midway between the planes of simple cubic lattice.

$$\Rightarrow \quad d_{110} = \frac{1}{2}\frac{a}{\sqrt{2}}.$$

The (1 1 1) planes of simple cubic lattice pass through the centre of all the faces of FCC lattice and hence no new planes arise in this case.

$$\Rightarrow \quad d_{111} = \frac{a}{\sqrt{3}}.$$

Body centred cubic lattice: In BCC lattice one unit is situated at each corner and one at the centre of the cubic. An additional (1 0 0) plane arises half way between (1 0 0) planes of a simple cubic frame.

$$\Rightarrow \quad d_{100} = \frac{1}{2}a$$

The (1 1 0) plane is the same as in a simple cubic lattice.

$$\Rightarrow \quad d_{110} = \frac{1}{2}\frac{a}{\sqrt{2}}.$$

The (1 1 1) plane of a BCC lattice lies midway between the (1 1 1) planes of a simple cubic lattice.

$$\Rightarrow \quad d_{111} = \frac{1}{2}\frac{a}{\sqrt{3}}.$$

10. Find the Miller indices of a set of parallel planes which make intercepts in the ratio of $2a : 3b$ on the x and y axis and are parallel to z-axis; $\vec{a}, \vec{b}, \vec{c}$ being primitive vectors of the lattice. Also calculate the interplanar distance d of the planes taking the lattice to be a cube with $a = b = c = 3$Å.

Soln. Intercept on the x-axis $= 2a$
Intercept on the y-axis $= 2b$
Intercept on the z-axis $= \infty$ (as the set of planes is parallel to z-axis)

The reciprocals of the numbers 2, 3 and ∞ are $\frac{1}{2}, \frac{1}{3}, \frac{1}{\infty}$ (or zero) respectively.

The smallest three integers having the same ratio are 3, 2, 0
Therefore, Miller indices $(h\,k\,l)$ are (3 2 0).
Lattice constant $a = b = c = 3$ Å

Therefore, interplanar distance $d = \frac{a}{\sqrt{h^2 + k^2 + \ell^2}} = \frac{3\text{Å}}{\sqrt{3^2 + 2^2 + 0^2}} = \frac{3}{\sqrt{13}}$ Å.

11. The distance between the adjacent atomic planes in $CaCO_3$ is 0.3 nm. The smallest Bragg scattering for 0.03 nm X-ray is **[GATE 2001]**

(a) 2.9° (b) 1.5° (c) 0.29° (d) 5.8°

Soln. Here, interatomic distance, $d = 0.3$ nm

Wavelength of X-ray is, $\lambda = 0.03$ nm

From Bragg's law : $n\lambda = 2d \sin\theta$

$$\Rightarrow \quad \sin\theta = \frac{\lambda}{2d} \qquad (\because \text{ smallest scattering is considered hence we have taken } n = 1)$$

$$\Rightarrow \quad \sin\theta = \frac{0.03\text{ nm}}{2 \times 0.3\text{ nm}} = \frac{0.03}{0.6} = \frac{1}{20}$$

$$\Rightarrow \quad \theta = \sin^{-1}\left(\frac{1}{20}\right) = \sin^{-1}(0.05)$$

$$\Rightarrow \quad \theta = 2.86° \simeq 2.9°$$

Hence, correct option is (a).

12. For a NaCl crystal, the cell-edge $a = 0.563$ nm. The smallest angle at which Bragg reflection can occur corresponds to a set of planes whose indices are **[GATE 2002]**

(a) (100) (b) (110) (c) (111) (d) (200)

Soln. For cubic system, the relation between interatomic distance (d) and cell-edge (a) is given by

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \text{where, } (hkl) = \text{miller indices} \qquad \ldots (i)$$

From Bragg's law : $2d \sin\theta = n\lambda$ ... (ii)

$$\therefore \quad \sin\theta = \frac{n\lambda}{2d}$$

For minimum θ, $n = 1$, d must be maximum.

For maximum d, $\sqrt{(h^2 + k^2 + l^2)}$ will be minimum. According to given options only "(a) (100)" shows mini-

mum $\sqrt{(h^2+k^2+l^2)}$, which gives smallest θ.

Hence, correct option is (a).

13. Silicon has diamond structure with until-cell-edge $a = 0.542$ nm. The interatomic separation is
(a) 0.122 nm (b) 0.234 nm (c) 0.383 nm (d) 0.542 nm **[GATE 2002]**

Soln. Unit-cell-edge $(a) = 0.542$ nm

The interatomic separation $(d) = ?$

Since diamond has fcc structure : $4r = a\sqrt{2}$

$$2r = \frac{a\sqrt{2}}{2} = \frac{a \times 1.414}{2} = 0.707 \times 0.542$$

$$\Rightarrow \quad d = 2r = 0.383 \text{ nm}$$

$r = \frac{a}{2\sqrt{2}}$

$\frac{0.542}{1.414} = 0.383$ nm.

$d = 2r = 0.383$ nm

Hence, correct option is (c).

14. If the ionic radii of Mn and S are 0.80 and 0.184 nm respectively, the structure of MnS will be
(a) Cubic closed packed (b) Body-centered cubic **[GATE 2003]**
(c) NaCl type (d) Primitive cubic cell

Soln. Ionic solid MnS will have NaCl type crystal structure.

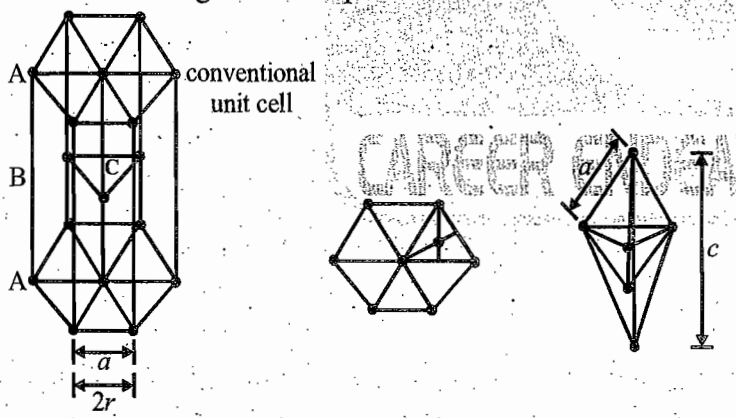
Hence, correct option is (c).

15. The c/a ratio for an ideal hexagonal closed packed structure is **[GATE 2004]**

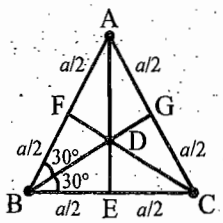
(a) $\frac{2}{\sqrt{3}}$ (b) $\sqrt{8}$ (c) $\sqrt{5}$ (d) $\sqrt{\frac{8}{3}}$

Soln. Let a is interatomic distance within a layer and c is height of the unit cell

Unit cell of hexagonal closed packed structure can be made as:



From this figure, $\frac{c}{a} = \sqrt{\frac{8}{3}}$.



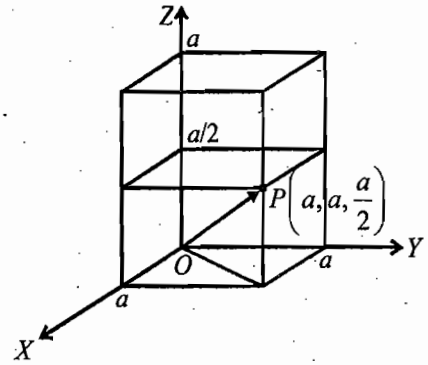
In figure : $BD = \frac{a/2}{\cos 30°} = \frac{a/2}{\sqrt{3}/2} = \frac{a}{\sqrt{3}}$

In the center of spheres in contact, then

$$a^2 = \left(\frac{c}{2}\right)^2 + \left(\frac{a}{\sqrt{3}}\right)^2 \Rightarrow a^2 - \frac{a^2}{3} = \frac{c^2}{4} \Rightarrow \frac{2a^2}{3} = \frac{c^2}{4} \Rightarrow \frac{c}{a} = \sqrt{\frac{8}{3}} = 1.633.$$

Hence, correct option is (d).

16. In crystallographic notations the vector $\overline{OP}$ in the cubic shell in the figure is **[GATE 2005]**



(a) [221] (b) [122] (c) [121] (d) [112]

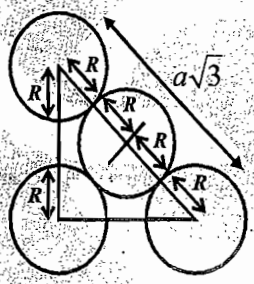
Soln. $\overline{OP} = \left[a, a, \frac{a}{2}\right] = \left[11\frac{1}{2}\right] = [221].$

Hence, correct option is (a).

17. For a closed packed bcc structure of hard spheres, the lattice constant a is related to the sphere radius R as

(a) $a = \frac{4R}{\sqrt{3}}$ (b) $a = 4R\sqrt{3}$ (c) $a = 4R\sqrt{2}$ (d) $a = 2R\sqrt{2}$ **[GATE 2005]**

Soln. For body centered cubic (bcc) structure, the atoms will lie at corners as well as body centers of cube.



From the figure, $4R = a\sqrt{3} \Rightarrow R = \frac{a\sqrt{3}}{4} \Rightarrow a = \frac{4R}{\sqrt{3}}$.

Hence, correct option is (a).

18. The powder diffraction pattern of a body centered cubic crystal is recorded by using CuK_α X-rays of wavelength 1.54 Å. **[GATE 2006]**

(A) If the (002) planes diffract at 60°, then lattice parameter is
(a) 2.67 Å (b) 3.08 Å (c) 3.56 Å (d) 5.34 Å

(B) Assuming the atomic mass of the constituent atoms to be 50.94 amu, then density of the crystal in units of kg/m^3 is
(a) 3.75×10^3 (b) 4.45×10^3 (c) 5.79×10^3 (d) 8.89×10^3

Soln. **(A)** $(hkl) = (002)$, $\theta = 60°$, $\lambda = 1.54$ Å

From equation, $d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{a}{\sqrt{0^2 + 0^2 + 2^2}} = \frac{a}{\sqrt{4}} = \frac{a}{2}$

From Bragg's law, $2d \sin\theta = n\lambda$

$\Rightarrow \quad 2 \times \frac{a}{2} \times \sin 60° = 1 \times 1.54 \text{ Å}$ (Taking first order reflections, $n = 1$)

$\Rightarrow \quad a = \frac{1 \times 1.54 \times 2}{\sqrt{3}} = 1.78 \text{ Å}$ (No option matches the result)

By taking second order reflections i.e., $n = 2$: $a = \frac{2 \times 1.54 \times 2}{\sqrt{3}} = 3.556 \text{ Å} \cong 3.56 \text{ Å}$

Hence, correct option is (c).

(B) Density of the crystal $(\rho) = \frac{nM}{Na^3} = \frac{2 \times 50.94}{6.023 \times 10^{26} \times (3.56 \times 10^{-10})^3} \text{ kg/m}^3$

$= 0.3749 \times 10^4 \text{ kg/m}^3$

$= 3.75 \times 10^3 \text{ kg/m}^3$

Hence, correct option is (a).

19. Consider the atomic packing factor (APF) of the following crystal : P : simple cubic, Q : Body centered cubic, R : Face centered cubic, S : Diamond, T : Hexagonal close packed. Which two of the above structures have equal APF ? **[GATE 2007]**

Soln.

Crystal structure	APF
P : Simple cubic	52%
Q : Body-centered cubic	68%
R : Face-centered cubic	74%
S : Diamond	34%
T : Hexagonal close packed	74%

From above table, it is clear that, the APF of face-centered cubic (R) and hexagonal close packed (T) are same.

Hence, correct option is (d).

20. In a powder diffraction pattern recorded from a face-centered cubic sample using X-rays, the first peak appears at 30°. The second peak will appear at **[GATE 2007]**

(a) 32.8° (b) 33.7° (c) 34.8° (d) 35.3°

Soln. For face-centered cubic sample, $\theta_1 = 30°$, $\theta_2 = ?$

For first peak, $(hkl) = (111)$

For second peak, $(hkl) = (200)$

Therefore, from Bragg's law: $2d \sin\theta = \lambda$

$\Rightarrow \quad \frac{2a}{\sqrt{h^2 + k^2 + l^2}} \sin\theta = \lambda$ ... (i)

For first peak ; $\frac{2a}{\sqrt{h^2 + k^2 + l^2}} \sin\theta_1 = \lambda \Rightarrow \lambda = \frac{2a \sin\theta}{\sqrt{1^2 + 1^2 + 1^2}}$

$\Rightarrow \quad \lambda = \frac{2a \sin 30°}{\sqrt{3}} = \frac{a}{\sqrt{3}}$ ... (ii)

For second peak ; $\frac{2a}{\sqrt{2^2+0^2+0^2}}\sin\theta_2 = \lambda \Rightarrow \lambda = \frac{2a\sin\theta_2}{\sqrt{4}}$

$\Rightarrow \lambda = a\sin\theta_2$ ... (iii)

Therefore, from equations (ii) and (iii), we get, $a\sin\theta_2 = \frac{a}{\sqrt{3}} \Rightarrow \sin\theta_2 = \frac{1}{1.732} = 0.577$

$\Rightarrow \theta_2 = \sin^{-1}(0.5773) = 35.26°$

Hence, correct option is (d).

21. A metal with body centered cubic (bcc) structure shows the first (i.e. smallest angle) diffraction peak at a Bragg angle of $\theta = 30°$. The wavelength of X-ray used is 2.1 Å. The volume of the unit cell of the metal is

(a) 26.2 (Å)^3 (b) 13.1 (Å)^3 (c) 9.3 (Å)^3 (d) 4.6 (Å)^3 **[GATE 2011]**

Soln. Given that : $\lambda = 2.1$ Å, $\theta = 30°$, bcc structure

From Bragg's law : $2d\sin\theta = \lambda \Rightarrow d = \frac{\lambda}{2\sin\theta} = \frac{2.1\text{ Å}}{2\times\sin 30°} = \frac{2.1\text{ Å}}{2\times\frac{1}{2}} = 2.1\text{ Å}.$

For first diffraction peak $(hkl) = (100)$

$\because\ d = \frac{a}{\sqrt{h^2+k^2+l^2}} \Rightarrow a = d\times\sqrt{h^2+k^2+l^2} \Rightarrow a = 2.1\text{ Å}\times\sqrt{1^2+0^2+0^2} \Rightarrow a = 2.1\text{ Å}$

$\therefore$ Volume of the unit cell $= a^3 = (2.1\text{ Å})^3 = 9.3\text{ (Å)}^3$

Hence, correct option is (c).

22. A simple cubic crystal with lattice parameter a_c under goes transition into a tetragonal structure with lattice parameters $a_t = b_t = \sqrt{2}\,a_c$ and $c_t = 2a_c$, below a certain temperature. The ratio of the interplanar spacings of (101) planes for the cubic and the tetragonal structures is **[GATE 2012]**

(a) $\sqrt{\frac{1}{6}}$ (b) $\frac{1}{6}$ (c) $\sqrt{\frac{3}{8}}$ (d) $\frac{3}{8}$

Soln. Relation between lattice parameters : a, b and c; and interplanar spacings of (hkl) plane is given by

$$d_{hkl} = \frac{1}{\sqrt{\left(\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}\right)}} \quad \text{... (i)}$$

For simple cubic crystal, $a = b = c = a_c$, $d_{(101)} = ?$

$$\therefore\ d_{hkl} = (d_{101})_c = \frac{1}{\sqrt{\frac{1^2}{a_c^2}+\frac{0^2}{a_c^2}+\frac{1^2}{a_c^2}}} = \frac{1}{\sqrt{\frac{2}{a_c^2}}} = \frac{a_c}{\sqrt{2}} \quad \text{... (ii)}$$

For tetragonal crystal, $a_t = b_t = \sqrt{2}\,a_c$, $c_t = 2a_c$

$$\therefore \quad d_{hkl} = (d_{101})_t = \frac{1}{\sqrt{\frac{1^2}{\left(\sqrt{2}\,a_c\right)^2} + \frac{0^2}{\left(\sqrt{2}\,a_c\right)^2} + \frac{1^2}{\left(2a_c\right)^2}}}$$

$$= \frac{1}{\sqrt{\frac{1}{2a_c^2} + \frac{1}{4a_c^2}}} = \frac{1}{\sqrt{\frac{3}{4a_c^2}}} = \frac{2a_c}{\sqrt{3}} \qquad \text{... (iii)}$$

$$\therefore \quad \frac{(d_{101})_c}{(d_{101})_t} = \frac{\frac{a_c}{\sqrt{2}}}{\frac{2a_c}{\sqrt{3}}} = \frac{\sqrt{3}\,a_c}{2\sqrt{2}\,a_c} = \sqrt{\frac{3}{8}}.$$

Hence, correct option is (c).

23. The miller indices of a plane passing through the three points having coordinates (0, 0, 1), (1, 0, 0) and $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{4}\right)$ are **[GATE 2014]**

(a) (2 1 2) (b) (1 1 1) (c) (1 2 1) (d) (2 1 1)

Soln. Let the plane is $\frac{x}{OA} + \frac{y}{OB} + \frac{z}{OC} = 1$, where OA, OB and OC are intercepts on x, y and z-axis respectively.

Now, for (hkl) plane, $OA = \frac{a}{h}$, $OB = \frac{a}{k}$, $OC = \frac{a}{l}$

Thus above equation implies that $\frac{xh}{a} + \frac{yk}{a} + \frac{zl}{a} = 1$

$\Rightarrow \quad xh + yk + zl = a$

For (1, 0, 0), $ah = a \Rightarrow h = 1$

For (0, 0, 1), $al = a \Rightarrow l = 1$

For $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{4}\right)$, $\frac{a}{2}\cdot h + \frac{a}{2}\cdot k + \frac{a}{4}\cdot l = a \Rightarrow \frac{a}{2}\cdot 1 + \frac{a}{2}\cdot k + \frac{a}{4}\cdot 1 = a \Rightarrow k = \frac{1}{2}$

Thus, $(hkl) = \left(1\,\frac{1}{2}\,1\right) = (2\,1\,2)$

Hence, correct option is (a).

24. The lattice parameters a, b, c of an orthorhombic crystal are related by $a = 2b = 3c$. In units of a, the interplanar separation between the (110) planes is_____ (upto three decimal places). **[GATE 2015]**

Soln. Lattice parameters a, b, c have relation $a = 2b = 3c$

$$\Rightarrow \quad a = a,\ b = \frac{a}{2},\ c = \frac{a}{3}$$

and the miller indices of the plane $(hkl) = (110)$ i.e., $h = 1,\ k = 1,\ l = 0$

$$\therefore \text{ Interplanar separation } d = \frac{1}{\sqrt{\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}}} = \frac{1}{\sqrt{\frac{1^2}{a^2}+\frac{1^2}{\left(\frac{a}{2}\right)^2}+\frac{0^2}{\left(\frac{a}{3}\right)^2}}}$$

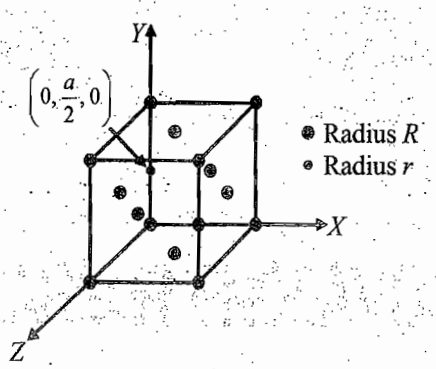
$$= \frac{1}{\sqrt{\frac{1}{a^2}+\frac{4}{a^2}+\frac{0}{a^2}}} = \frac{1}{\sqrt{\frac{5}{a^2}}} = \frac{a}{\sqrt{5}} = 0.447a$$

Hence, correct answer is 0.477 *a*.

25. Atoms, which can be assumed to be hard spheres of radius R, are arranged in an fcc lattice with lattice constant a, such that each atom touches its nearest neighbours. Take the centre of one of the atoms as origin. Another atom of radius r (assumed to be hard sphere) is to be accommodated at a position $\left(0, \frac{a}{2}, 0\right)$ without distorting the lattice. The maximum value of $\frac{r}{R}$ is _____ (Give your answer upto two decimal places).

[GATE 2016]

Soln. Along the Y-axis there are three atoms [Two at corners and one at $\left(0, \frac{a}{2}, 0\right)$]. If a is the lattice parameters.



Then $a = 2R + 2r$ ... (i)

Diagonal of each face will have 4 atoms (two at corners and one at center).

$\therefore \sqrt{2}a = 4R$ ... (ii)

$\Rightarrow R = \frac{\sqrt{2}a}{4}$

Now putting value of R from equation (ii) to equation (i), we get $a = 2\left(\frac{\sqrt{2}a}{4}\right) + 2r$

$\Rightarrow 2r = a - \left(\frac{2\sqrt{2}a}{4}\right) = \left[\frac{4-2\sqrt{2}}{4}\right]a$

$\Rightarrow r = \left(\frac{4-2\sqrt{2}}{8}\right)a$ ... (iii)

$$\therefore \quad \frac{r}{R} = \frac{\left(\frac{4-2\sqrt{2}}{8}\right)a}{\left(\frac{\sqrt{2}a}{4}\right)} = \frac{4}{8} \times \frac{\left(4-2\sqrt{2}\right)}{\sqrt{2}} = \frac{2\left(2-\sqrt{2}\right)}{2\sqrt{2}} = \frac{2\sqrt{2}\left(\sqrt{2}-1\right)}{2\sqrt{2}} = \sqrt{2}-1 = 1.414-1 = 0.414.$$

Hence, correct answer is (0.41).

26. The second order maximum in the diffraction of X-rays of 0.20 nanometer wavelength from a simple cubic crystal is found to occur at an angle of thirty degrees to the crystal plane. The distance between the lattice planes is

(a) 1 Angstrom (b) 2 Angstrom (c) 4 Angstrom (d) 8 Angstrom **[JEST-2012]**

Soln. Given: $n = 2$, $\lambda = 0.20$ nanometer, $\theta = 30^\circ$, $d = ?$

From Bragg's law: $2d \sin\theta = n\lambda$

$\Rightarrow \quad 2 \times d \times \sin 30^\circ = 2 \times 0.20$ nanometer

$$\Rightarrow \quad d = \frac{2 \times 0.20}{2 \times \sin 30^\circ} = \frac{2 \times 0.20}{2 \times \frac{1}{2}} = 0.40 \text{ nanometer}$$

$\Rightarrow \quad d = 4$ Angstrom

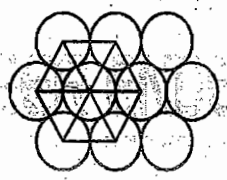
i.e., the distance between the lattice planes is 4 Angstrom.

Hence, correct option is (c).

27. A flat surface is covered with non-overlapping disks of same size. What is the largest fraction of the area that can be covered ?

(a) $\frac{3}{\pi}$ (b) $\frac{5\pi}{6}$ (c) $\frac{6}{7}$ (d) $\frac{\pi}{2\sqrt{3}}$ **[JEST-2013]**

Soln. Let the radius of the circular disk is a. Then, area of the circular disk $= \pi r^2$



Here, centers of three disks make an equilateral triangle with area $= \frac{\sqrt{3}a^2}{4} = \frac{\sqrt{3}(2r)^2}{4}$.

Therefore, packing fraction of the triangular lattice $= \left(\frac{\frac{3}{6} \times \pi r^2}{\frac{\sqrt{3}a^2}{4}}\right) = \left(\frac{\frac{3}{6} \times \pi r^2}{\frac{\sqrt{3} \times (2r)^2}{4}}\right) = \frac{\pi}{2\sqrt{3}}$.

Therefore, the fractional area of the flat surface that can be covered by these circular discs $= \frac{\pi}{2\sqrt{3}}$.

Hence, correct option is (d).

28. A metal suffers a structural phase transition from face-centered cubic (FCC) to the simple cubic (SC) structure. It is observed that this phase transition does not involve any change of volume. The nearest neighbour distances d_{fcc} and d_{sc} for the FCC and the SC structures respectively are in the ratio (d_{fcc}/d_{sc}) [Given: $2^{1/3} = 1.26$]
(a) 1.029 (b) 1.122 (c) 1.374 (d) 1.130 **[JEST-2013]**

Soln. For FCC crystal strucutre, the nearest neighbour distance, $d_{fcc} = \frac{\sqrt{2}}{2} a_{fcc}$ ... (i)

For SC crystal strucutre, the nearest neighbour distance, $d_{sc} = a_{sc}$ ... (ii)
Since, volume does not change in this phase transformation from FCC to SC structure.
Therefore, density of FCC structure = density of SC structure

i.e., $\frac{4}{a_{fcc}^3} = \frac{1}{a_{sc}^3}$

$\Rightarrow \frac{a_{fcc}^3}{a_{sc}^3} = 4 \Rightarrow \frac{a_{fcc}}{a_{sc}} = (4)^{1/3} = (2)^{2/3}$ ... (iii)

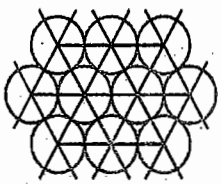
Now, from equations (i) and (ii), we get

$$\frac{d_{fcc}}{d_{sc}} = \frac{\left(\frac{\sqrt{2}}{2} a_{fcc}\right)}{a_{sc}} = \frac{1}{\sqrt{2}} \times \frac{a_{fcc}}{a_{sc}} = \frac{1}{\sqrt{2}} \times (2)^{2/3} = \frac{(2)^{2/3}}{(2)^{1/2}} = (2)^{\frac{2}{3}-\frac{1}{2}} = (2)^{\frac{1}{6}} = (2^{\frac{1}{3}})^{\frac{1}{2}} = (1.26)^{\frac{1}{2}} = 1.122.$$

Hence, correct option is (b).

29. Circular discs of radius 1 m each are placed on a plane so as to form a closely packed triangular lattice. The number of discs per unit area is approximately equal to
(a) 0.86 m^{-2} (b) 0.43 m^{-2} (c) 0.29 m^{-2} (d) 0.14 m^{-2} **[JEST-2014]**

Soln. Given, radius of circular disc $r = 1$ m



The circular discs will form a equilateral triangular lattice of side $a = 2r = 2 \times 1\text{ m} = 2\text{ m}$, where r is the radius of the circular discs.

Now, area of the triangular lattices $= \frac{\sqrt{3}}{4} a^2 = \frac{\sqrt{3}}{4} \times (2r)^2 = \sqrt{3} r^2 = \sqrt{3}(1)^2 = \sqrt{3}\text{ m}^2$

Number of circular discs inside the triangular lattice $= \frac{1}{6} \times 3 = 0.5$.

Therefore, number of discs/area $= \frac{0.5}{\sqrt{3}} = \frac{0.5}{\sqrt{3}}\text{ m}^{-2} = 0.28867 = 0.29\text{ m}^{-2}$

Hence, correct option is (c).

30. The number of different Bravais lattices possible in two dimension is
(a) 2 (b) 3 (c) 5 (d) 6 **[JEST-2016]**

Soln. The number of different Bravais lattices possible in two dimension is 5. The lattices are oblique $(a \neq b, \gamma \neq 90°)$, square $(a = b, \gamma = 90°)$, primitive rectangular $(a \neq b, \gamma = 90°)$, non-primitive rectangular $(a \neq b, \gamma = 90°)$ and hexagonal $(a = b, \gamma = 120°)$.
Hence, correct option is (c).

PRACTICE SET

1. The distance of first nearest neighbours in the BCC lattice is

(a) $\frac{a}{\sqrt{2}}$ (b) a (c) $a\sqrt{2}$ (d) $\frac{\sqrt{3}a}{2}$

2. The atomic packing fraction of diamond cubic lattice is

(a) 60% (b) 34% (c) 74% (d) 52%

3. If (326) are the miller indices of a plane, the intercepts made by the plane on the three crystallographic axes are

(a) $(2a, 3b, c)$ (b) (a, b, c) (c) $(a, 2b, 3c)$ (d) none of these

4. A plane intercepts at $a, \frac{b}{2}, 3c$ in a simple cubic unit cell. The miller indices of the plane are

(a) (132) (b) (261) (c) (361) (d) (123)

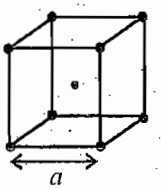
5. The Miller indices of the plane parallel to the x and y axes are

(a) (100) (b) (010) (c) (001) (d) (111)

6. In a simple cubic lattice, the ratio $d_{100} : d_{110} : d_{111}$ is

(a) $6:\sqrt{3}:2$ (b) $6:3:\sqrt{2}$ (c) $\sqrt{6}:\sqrt{3}:\sqrt{2}$ (d) $\sqrt{6}:\sqrt{3}:1$

7. The conventional unit cell of a body centered cubic Bravais lattice is shown in the figure below. The conventional cell has volume a^3. What is the volume of the primitive unit cell?



(a) $\frac{a^3}{8}$ (b) $\frac{a^3}{4}$ (c) $\frac{a^3}{2}$ (d) a^3

8. In a simple cubic lattice a = 2Å, then the planar atomic density of (100) plane is

(a) 10^{15} atoms/cm^2 (b) 2.5×10^{15} atoms/cm^2
(c) 5×10^{15} atom/cm^2 (d) 7.5×10^{15} atoms/cm^2

9. The number of lattice points in a primitive cell is

(a) 2 (b) 3 (c) 1 (d) 4

10. If n is the number of atoms in the unit cell of the cubic system, N and M are the Avogadro's number and atomic weight respectively and ρ is the density of the element then the lattice constant a is given by

(a) $\left(\frac{M\rho}{nN}\right)^{1/3}$ (b) $\left(\frac{nM}{N\rho}\right)^{1/3}$ (c) $\left(\frac{nN}{M\rho}\right)^{1/3}$ (d) $\left(\frac{\rho N}{Mn}\right)^{1/3}$

11. Magnesium has HCP structure. The radius of magnesium atom is 0.1605 nm. The volume of unit cell of magnesium is

(a) $0.7\times10^{-28} m^3$ (b) $2.8\times10^{-28} m^3$ (c) $1.4\times10^{-28} m^3$ (d) $0.35\times10^{-28} m^3$

12. The spacing $d_{hk\ell}$ of the planes $(hk\ell)$ in a tetragonal crystal is

(a) $\left(\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{\ell^2}{c^2}\right)^{-1/2}$ (b) $\left(\frac{h^2+k^2}{a^2}+\frac{\ell^2}{c^2}\right)^{-1/2}$

(c) $\left[\frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right)+\frac{\ell^2}{c^2}\right]^{-1/2}$ (d) $a\left(h^2+k^2+\ell^2\right)^{-1/2}$

13. For a fcc lattice the ratio of $d_{200} : d_{220} : d_{222}$ is

(a) $\sqrt{3}:\sqrt{6}:\sqrt{2}$ (b) $1:\sqrt{2}:\sqrt{6}$ (c) 1 : 2 : 3 (d) $\sqrt{6}:\sqrt{3}:\sqrt{2}$

14. For a given cubic crystal lattice parameter a is 3.18Å. The d spacing for (111) plane is

(a) 2.25Å (b) 1.84Å (c) 3.18Å (d) 3.90Å

15. The number of lattice points in a BCC unit cell is

(a) 1 (b) 2 (c) 3 (d) 4

ANSWER KEY

1. (d)	**2. (b)**	**3. (a)**	**4. (c)**	**5. (c)**	**6. (c)**	**7. (c)**
8. (b)	**9. (c)**	**10. (b)**	**11. (c)**	**12. (b)**	**13. (d)**	**14. (b)**
15. (b)						

Chapter 2

RECIPROCAL LATTICE & X-RAY DIFFRACTION

Reciprocal lattice:

Every crystal has two lattices associated with it, the crystal lattice (or direct space lattice) and the reciprocal lattice.

The concept of reciprocal lattice was introduced for the purpose of tabulating two important properties of crystal planes : their slope and their interplanar spacing.

Each set of parallel planes in a direct lattice can be represented by a normal to these planes having length equal to the reciprocal of the interplanar spacing. The normals are drawn with reference to any arbitrary origin and points are marked at their ends. These points form a regular arrangement which is called reciprocal lattice. Thus each point in a reciprocal lattice is a representative point of a particular set of parallel planes. It is easier to deal with such points than to deal with set of planes. That's why we use reciprocal lattice.

Thus reciprocal lattice vector is a vector whose magnitude is equal to the reciprocal of the interplanar spacing i.e., $\frac{1}{d_{hkl}}$ and direction is parallel to the normal to $(h\,k\,l)$ plane.

Why reciprocal lattice is so named? The reciprocal lattice is so named because the length assigned to each normal representing the reciprocal lattice is proportional to the reciprocal of the interplanar spacing of the plane in ordinary space.

Primitive translation vectors of reciprocal lattice:

Let $\vec{a}, \vec{b}, \vec{c}$ be the primitive translation vectors of a direct space lattice for a crystal. Consider a unit cell.

The volume of this unit cell is given by

$$V = \vec{a}.\left(\vec{b}\times\vec{c}\right) = \vec{b}.\left(\vec{c}\times\vec{a}\right) = \vec{c}.\left(\vec{a}\times\vec{b}\right)$$

The vectors given by $\vec{A} = 2\pi\frac{\vec{b}\times\vec{c}}{\vec{a}.\left(\vec{b}\times\vec{c}\right)};\ \vec{B} = 2\pi\frac{\vec{c}\times\vec{a}}{\vec{b}.\left(\vec{c}\times\vec{a}\right)};\ \vec{C} = 2\pi\frac{\vec{a}\times\vec{b}}{\vec{c}.\left(\vec{a}\times\vec{b}\right)}$

are known as reciprocal lattice vectors or primitive translation vectors of reciprocal lattice.

$$\vec{A}.\vec{a} = 2\pi,\ \vec{A}.\vec{b} = 0 \text{ and } \vec{A}.\vec{c} = 0$$

$$\Rightarrow \quad \vec{B}.\vec{a} = 0,\ \vec{B}.\vec{b} = 2\pi \text{ and } \vec{B}.\vec{c} = 0$$

$$\Rightarrow \quad \vec{C}.\vec{a} = 0,\ \vec{C}.\vec{b} = 0 \text{ and } \vec{C}.\vec{c} = 2\pi$$

Choosing $\vec{A}, \vec{B}$ and $\vec{C}$ as the primitive translation vectors of the reciprocal lattice (also known as reciprocal axes) we can construct the reciprocal lattice points or reciprocal lattice vectors given by

$$\vec{G} = h\vec{A} + k\vec{B} + l\vec{C}$$

where h, k, l are intergers and define the coordinate of the point in the reciprocal space.

The crystal lattice is a lattice in real or ordinary space whereas reciprocal lattice is a lattice in the reciprocal space or associated $\vec{k}$ -space or Fourier space. The wave vector $\vec{k}$ is always drawn in Fourier space. Vectors in the crystal lattice have dimensions of length i.e., $[L^1]$ and vectors in the reciprocal lattice have dimensions of $\frac{1}{(\text{Length})}$ i.e., $[L^{-1}]$.

Properties of reciprocal lattice:

(i) The direct lattice is the reciprocal lattice to its own reciprocal lattice. Simple cubic lattice is self reciprocal whereas BCC and FCC lattices are reciprocal of each other.

(ii) Each point in a reciprocal lattice corresponds to a particular set of parallel planes of the direct lattice.

(iii) The distance of a reciprocal lattice point from an arbitrarily fixed origin is inversely proportional to the interplanar spacing of the corresponding parallel planes of the direct lattice.

(iv) The unit cell of the reciprocal lattice is not necessarily a parallelopiped. We deal with the Wigner Seitz cell of the reciprocal lattice which constitutes the Brillouin zone.

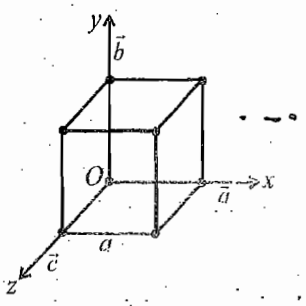
(v) The volume of a unit cell of the reciprocal lattice is inversely proportional to the volume of the corresponding unit cell of the direct lattice.

Reciprocal lattice of simple cubic lattice: Let the primitive translation vectors of a simple cubic cell be $\vec{a}, \vec{b}$ and $\vec{c}$. We can write the vectors as

$$\vec{a} = a\hat{i}, \vec{b} = a\hat{j} \text{ and } \vec{c} = a\hat{k}$$

The primitive translation vectors of the reciprocal of SC lattice are given by

$$\vec{A} = 2\pi \frac{(\vec{b} \times \vec{c})}{\vec{a}.(\vec{b} \times \vec{c})} = 2\pi \left(\frac{a\hat{j} \times a\hat{k}}{a^3} \right) = \frac{2\pi}{a} \hat{i}$$



Similarly, $$\vec{B} = 2\pi \frac{(\vec{c} \times \vec{a})}{\vec{b}.(\vec{c} \times \vec{a})} = 2\pi \left(\frac{a\hat{k} \times a\hat{i}}{a^3} \right) = \frac{2\pi}{a} \hat{j}$$

and $$\vec{C} = 2\pi \frac{(\vec{a} \times \vec{b})}{\vec{c}.(\vec{a} \times \vec{b})} = 2\pi \left(\frac{a\hat{i} \times a\hat{j}}{a^3} \right) = \frac{2\pi}{a} \hat{k}$$

Simple cubic lattice has side a and its reciprocal lattice has side $\left(\frac{2\pi}{a} \right)$.

Reciprocal of simple cubic lattice is also a simple cubic lattice with cube side $\left(\frac{2\pi}{a} \right)$ i.e., simple cubic lattice is self reciprocal lattice.

Volume of primitive unit cell of reciprocal lattice

$$V_R = \vec{A} \cdot (\vec{B} \times \vec{C}) \Rightarrow V_R = \left(\frac{2\pi}{a} \right)^3$$

Volume of reciprocal unit cell of any lattice is equal to $V_R = \frac{(2\pi)^3}{V_d}$, where V_d = volume of direct unit cell.

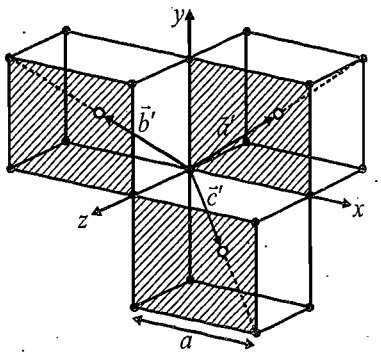
Reciprocal lattice of body centered cubic lattice:

Let the primitive translation vectors of a body centered cubic lattice are

$$\vec{a}' = \frac{a}{2}\left(\hat{i}+\hat{j}-\hat{k}\right),\ \vec{b}' = \frac{a}{2}\left(-\hat{i}+\hat{j}+\hat{k}\right),\ \vec{c}' = \frac{a}{2}\left(\hat{i}-\hat{j}+\hat{k}\right)$$

The primitive translation vectors of the reciprocal of body centered cubic lattice are given by

$$\vec{A} = 2\pi\frac{\vec{b}'\times\vec{c}'}{\vec{a}'.\left(\vec{b}'\times\vec{c}'\right)} = 2\pi\left(\frac{\frac{a^2}{2}\left(\hat{i}+\hat{j}\right)}{a^3/2}\right) = \frac{2\pi}{a}\left(\hat{i}+\hat{j}\right)$$



Similarly, $\vec{B} = 2\pi\frac{\vec{c}'\times\vec{a}'}{\vec{b}'.\left(\vec{c}'\times\vec{a}'\right)} = 2\pi\left(\frac{\frac{a^2}{2}\left(\hat{j}+\hat{k}\right)}{a^3/2}\right) = \frac{2\pi}{a}\left(\hat{j}+\hat{k}\right)$

$$\vec{C} = 2\pi\frac{\vec{a}'\times\vec{b}'}{\vec{c}'.\left(\vec{a}'\times\vec{b}'\right)} = 2\pi\left(\frac{\frac{a^2}{2}\left(\hat{k}+\hat{i}\right)}{a^3/2}\right) = \frac{2\pi}{a}\left(\hat{k}+\hat{i}\right)$$

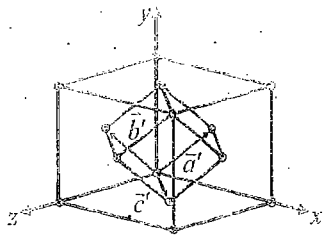
Hence, reciprocal of body centered cubic lattice is face centered cubic lattice with side $\left(\frac{4\pi}{a}\right)$.

Volume of reciprocal unit cell $V_R = \vec{A}\cdot\left(\vec{B}\times\vec{C}\right) \Rightarrow V_R = 2\left(\frac{2\pi}{a}\right)^3$.

Reciprocal lattice of face centered cubic lattice: Let the primitive translation vectors of a face centered cubic lattice are $\vec{a}' = \frac{a}{2}\left(\hat{i}+\hat{j}\right),\ \vec{b}' = \frac{a}{2}\left(\hat{j}+\hat{k}\right),\ \vec{c}' = \frac{a}{2}\left(\hat{k}+\hat{i}\right)$

The primitive translation vectors of the reciprocal of face centered cubic lattice are given by

$$\vec{A} = 2\pi\frac{\vec{b}'\times\vec{c}'}{\vec{a}'.\left(\vec{b}'\times\vec{c}'\right)} = 2\pi\left(\frac{\frac{a^2}{4}\left(\hat{i}+\hat{j}-\hat{k}\right)}{\frac{a^3}{4}}\right) = \frac{2\pi}{a}\left(\hat{i}+\hat{j}-\hat{k}\right)$$



Similarly, $\vec{B} = \frac{2\pi}{a}\left(-\hat{i}+\hat{j}+\hat{k}\right)$ and $\vec{C} = \frac{2\pi}{a}\left(\hat{i}-\hat{j}+\hat{k}\right)$

Hence, reciprocal of face-centered cubic lattice is body centred cubic lattice.

X-RAY DIFFRACTION:

What are X-rays:

Like visible light, X-rays are also a form of electromagnetic radiation having wavelength of the order of 1 Å. In other words, we can say that X-rays represent a relatively high energy form of radiation. In electromagnetic spectrum, X-rays lie between ultraviolet and gamma rays.

Production of X-rays:

The X-rays are produced when a stream of high energy charged particles, e.g. a beam of electrons are allowed to strike a metal target (such as Molybdenum, Copper or Tungsten) of high melting point. In this process electrons loose some of their energy which is converted into electromagnetic radiations, i.e. some part of energy will be converted into electromagnetic radiations of high frequency according to formula $\Delta E = h\nu$. These processes give continuous X-rays.

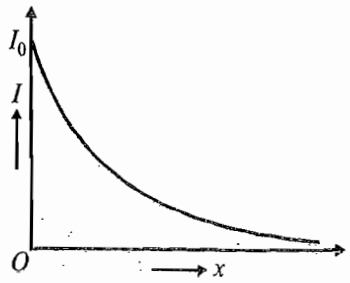
The wavelength of the X-rays can be given by $\Delta E = h\nu_{max} = \frac{hc}{\lambda_{min}}$.

$$\Rightarrow \quad \lambda_{min} = \frac{hc}{\Delta E} = \frac{12400}{E(\text{eV})} \text{ Å}$$

$$\Rightarrow \quad \lambda_{min} = \frac{12400}{V(\text{volt})} \text{ Å},$$

where V is the applied potential for accelerating the electrons.

Thus, we get $\lambda_{min} \propto \frac{1}{V}$.



Absorption of X-rays:

When X-rays of intensity (I_0) are passed through a material of absorption coefficient μ, the intensity of the transmitted beam is given by $I_t = I_0 e^{-\mu x}$, where x is the thickness of the material. Thus the intensity of X-ray beam decreases exponentially with the thickness of the absorbing material.

X-ray diffraction:

Similar to other electromagnetic radiatons, X-rays also interact with the electron cloud of the atoms. Since X-rays have shorter wavelengths, X-rays are scattered by adjacent atoms in crystal. The scattered X-rays interfere and give rise to diffraction phenomena. The atoms of crystal acts as a diffraction center for the X-rays like a three-dimensional diffraction grating. The X-ray diffraction pattern produced by this method can give us the information about the internal arrangement of atoms in crystals.

Consider parallel lattice planes equidistant from one another in a crystal structure, separated by a distance d. Suppose a beam of X-rays AB of wavelength λ is incident on a layer of atoms in one cleavage plane P of a crystal at a glancing angle θ at B and after reflection goes along BC. The ray DE incident on cleavage plane Q after reflection goes along EF. Draw BG perpendicular on DE and BH perpendicular on EF, then BG is the incident wave front and BH the reflected wave front.

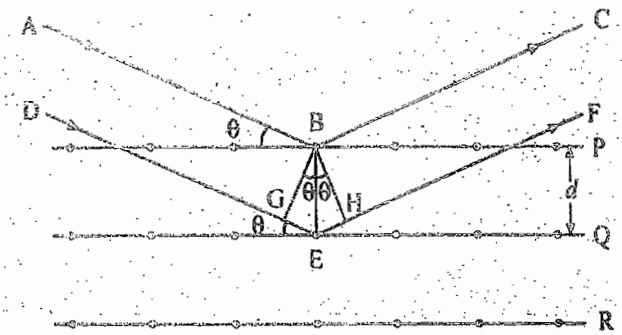
Path difference between the two wave fronts = GE + EH

Now, in ΔBGE, $GE = BE \sin\theta = d \sin\theta$ and in ΔBEH, $EH = BE \sin\theta = d \sin\theta$

Therefore, Path difference, $GE + EH = 2d \sin\theta$

If this path-difference is an integral multiple of wavelength λ, constructive interference will take place between the reflected beams. Thus the intensity will be maximum if

$$2d \sin\theta = n\lambda \qquad \text{where } n = 1, 2, 3, \ldots\ldots\ldots$$



Bragg's reflection of X-rays from the atomic planes

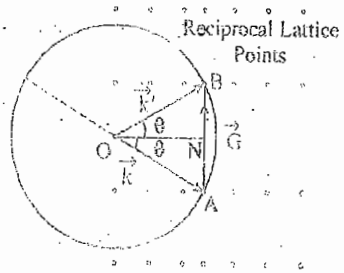
For $n = 1$, we get the first order spectrum and for $n = 2$, we get the second order spectrum and so on. This phenomenon is similar to that of the optical diffraction with diffraction grating with only the difference that here various parallel planes of the crystal act as lines in the grating. The above equation $2d \sin\theta = n\lambda$ is Bragg's equation and represents Bragg's law.

Physical significance of Bragg's law : The interpretation of Bragg's law gives that the diffraction intensities can be stronger only at certain values of θ for specific values of λ and d. Therefore, a knowledge of experimentally observed diffraction angles and wavelength of X-rays can provide the information about the interplanar spacing of the crystal. Thus, the space, shape and orientation of the unit cell can be determined from any diffraction experiment using monochromatic X-rays.

Ewald construction:

Ewald construction is a geometrical construction to get a relation between wave vector $\vec{k}$ and the direction of incident X-ray beam with the help of reciprocal lattice and thus derive Bragg's law in vector form. Draw a vector $\overrightarrow{OA} = \vec{k} = \frac{2\pi}{\lambda}$ in the direction of incident X-ray beam originating at O and terminating at any reciprocal lattice point A. Draw a sphere of radius $k = \frac{2\pi}{\lambda}$ with origin O as centre. This sphere is known as reflex sphere (The section of this sphere in a plane is a circle). Suppose this sphere intersects some point B of the reciprocal lattice whose indices are $(h'k'l')$, then $\overrightarrow{AB}$ represents the reciprocal lattice vector $\vec{G}$ and is normal to some set of direct lattice planes e.g., ON. $AB = |\vec{G}| = \frac{2\pi n}{d}$

where n is the largest integral factor common to numbers $(h'k'l')$ and d is the interplanar spacing for the set of parallel planes.



Ewald construction in the reciprocal lattice

Bragg's diffraction condition in terms of reciprocal lattice:

As the wave vector $\overrightarrow{OA} = \vec{k}$ is the incident wave vector, $\overrightarrow{OB} = \vec{k}'$ is the diffracted (or reflected) wave vector and is given by

$$\vec{k}' = \vec{k} + \vec{G} \qquad \ldots(i)$$

This shows that scattering changes only the direction of the wave vector $\vec{k}$ and the scattered wave vector differs from the incident wave vector by a reciprocal lattice vector $\vec{G}$.

For the diffraction, the magnitude of $(\vec{k} + \vec{G})$ must be equal to the wave vector $\vec{k}'$.

i.e. $$\vec{k}'^2 = (\vec{k} + \vec{G})^2 = (\vec{k} + \vec{G}) \circ (\vec{k} + \vec{G}) = \vec{k}^2 + 2\vec{k} \circ \vec{G} + \vec{G} \circ \vec{G}$$

But the magnitude of $\vec{k}'$ = magnitude of $\vec{k}$ ($\because$ wavelength of incident and scattered beam is same)

$\Rightarrow \qquad \vec{k}'^2 = \vec{k}^2$

Hence, equation (i) becomes.

$$2\vec{k}\cdot\vec{G}+\vec{G}\cdot\vec{G}=0 \qquad \Rightarrow \boxed{2\vec{k}\cdot\vec{G}+G^2=0}$$

$$\Rightarrow \qquad \left(\vec{k}+\frac{\vec{G}}{2}\right)\cdot\vec{G}=0$$

This is Bragg's law in vector form and gives the Bragg's diffraction conditions in terms of reciprocal lattice vector $\vec{G}$.

Brillouin zones : A Brillouin zone is the locus of all those $\vec{k}$- values in the reciprocal lattice which are Bragg reflected. For example, let us construct the Brillouin zones for a simple cubic structure with lattice parameter a. The primitive translation vectors of the simple cubic structure are

$$\vec{a}=a\hat{i},\ \vec{b}=a\hat{j} \qquad \text{... (i)}$$

The corresponding translation vectors of the reciprocal lattice are

$$\vec{A}=\left(\frac{2\pi}{a}\right)\hat{i},\ \vec{B}=\left(\frac{2\pi}{a}\right)\hat{j}$$

The reciprocal lattice vector is given by

$$\vec{G}=h\vec{A}+k\vec{B}=\frac{2\pi}{a}\left(h\hat{i}+k\hat{j}\right) \qquad \text{... (ii)}$$

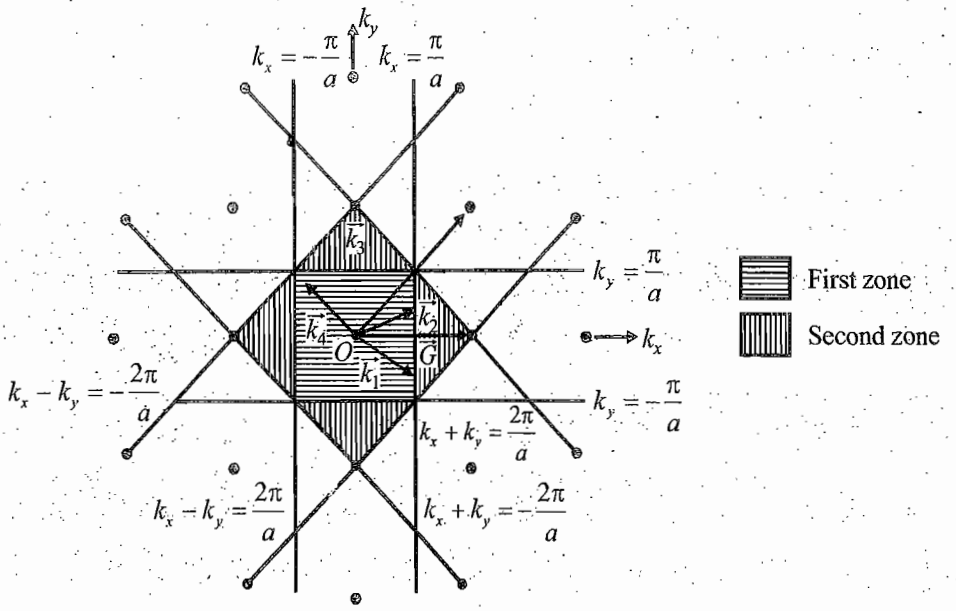
The Bragg's law in the reciprocal lattice is given by

$$2\vec{k}\cdot\vec{G}+G^2=0 \qquad \text{... (iii)}$$

$$\Rightarrow \ 2\left(\frac{2\pi}{a}\right)\left[\left(k_x\hat{i}+k_y\hat{j}\right)\cdot\left(h\hat{i}+k\hat{j}\right)\right]+\frac{4\pi^2}{a^2}\left(h^2+k^2\right)=0$$

$$\Rightarrow \ \frac{4\pi}{a}\left[hk_x+kk_y\right]=-\frac{4\pi^2}{a^2}\left(h^2+k^2\right)$$

$$\Rightarrow \ hk_x+kk_y=-\frac{\pi}{a}\left(h^2+k^2\right) \qquad \text{... (iv)}$$



Brillouin zones of a square lattice in its reciprocal lattice

The $\vec{k}$- values which are Bragg reflected are obtained by the all possible combinations of h and k.

For $h = \pm 1$ and $k = 0$, equation (iv) gives $k_x = \pm\frac{\pi}{a}$ and k_y is arbitrary.

Also, for $h = 0$ and $k = \pm 1$, equation (iv) gives $k_y = \pm\frac{\pi}{a}$ and k_x is arbitrary.

Thus, we get a square of side $\left(\frac{2\pi}{a}\right)$ bounded by $k_x = \pm\frac{\pi}{a}$ and $k_y = \pm\frac{\pi}{a}$. This square is called as first Brillouin zone. Hence, the first zone of a square lattice of side a is a square of side $\frac{2\pi}{a}$.

In addition to this set of lines, some other sets of lines are also possible which satisfies equation (iv). For example, $h = \pm 1$ and $k = \pm 1$, equation (iv) gives the following set of lines $\pm k_x \pm k_y = \frac{2\pi}{a}$. The area bounded by these four lines are called as second Brillouin zone. Similarly, we can construct other Brillouin zones. The boundaries of Brillouin zones represent the loci of $\vec{k}$- values that are Bragg reflected. Hence we consider them as reflecting planes. The boundaries of the first zone represent the reflecting planes for the first order reflection and those of the second zone represent the reflecting planes for the second order reflection, and so on. A $\vec{k}$- vector that does not terminate at a zone boundary can not produce Bragg reflection. So, we can say that Brillouin zone pattern can be used to determine the X-ray diffraction pattern of a crystal and vice-versa. The Brillouin zones for a three dimensional cubical lattice are constructed using the generalized equation

$$hk_x + kk_y + lk_z = -\frac{\pi}{a}\left(h^2 + k^2 + l^2\right)$$

where a is the length of the cube edge.

Thus, we get first Brillouin zone as a cube of side equal to $\left(\frac{2\pi}{a}\right)$. The second zone is formed by adding pyramids to each face of the cube (first zone) as triangles are added to the square in two-dimensions, and so on.

Electron diffraction : Similar to X-rays, a beam of electron can also be used to characterize the crystal structure. A beam of electron emitted from a hot wire (as a result of thermionic emission) is accelerated through vacuum under a very large electrode potential (V) and is then passed through a collimator before it gets diffracted by the specimen to be studied.

The energy (E) acquired by these electrons will depend on accelerating voltage (V), thus, $E = eV$ ... (i)

where e is electronic charge.

According to de-Broglie hypothesis, the wavelength of the moving electrons can be given by

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}} = \frac{h}{\sqrt{2meV}} \quad \text{... (ii)}$$

where m is the mass of electrons.

Putting $m = 9.11 \times 10^{-31}$ kg and $e = 1.6 \times 10^{-19} C$, the wavelength λ will be $\lambda = \left(\frac{150}{V}\right)^{1/2}$ Å $= \frac{12.24}{\sqrt{V}}$ Å.

Thus, wavelength of moving electron is inversely proportional to the square root of the accelerating voltage and hence can be varied easily to get the desired wavelength of electron beam.

Thus, if we apply the accelerating voltage (V) such that the wavelength of the electron beam become equal to the order of atomic distances, then we can use electron beam diffraction.

Neutron diffraction:

Neutron diffraction is other diffraction technique that can be employed at the place of X-ray and electron diffraction.

The wavelength of neutron is given by

$$\lambda_n = \frac{h}{p} = \frac{h}{\sqrt{2m_n E}} \qquad \ldots (i)$$

Since neutrons are neutral particles, so the neutrons can not be accelerated by applying potential. The neutrons can be accelerated thermally. The kinetic energy of a neutron is given by

$$E = \frac{3}{2}k_B T \qquad \ldots (ii)$$

Thus, the wavelength $\lambda_n = \frac{h}{\sqrt{3m_n k_B T}} \Rightarrow \lambda_n \propto \frac{1}{\sqrt{T}}$.

If temperature of the neutrons is selected such that the wavelength of neutron becomes equal to the order of atomic distances, then these neutrons can be used in diffraction phenomena.

Diffraction intensity:

The different directions of the diffracted X-ray beam obtained according to Bragg's law are governed by the geometry and the size of the unit cell. These directions will not be affected by the arrangement of atoms associated with each lattice point of the crystal structure. However, the complexity of the atomic structure within the unit cell does affect the intensity of the diffracted beam. The intensity depends on the atomic scattering factor, the position of each atom in unit cell. Since, the electrons are the only component that an atom have, therefore, the X-rays scattered from one part of an atom interfere with those scattered from the other part at all angles of scattering. Since, the electrons are distributed throughout the atomic volume, the diffracted beams are obtained as a result of combination of the scattered waves from the electrons of all atoms in the unit cell. This process involves two distinct contributions.

1. Scattering from electrons in the same atom. This gives the atomic scattering factor f.
2. The summation of this scattering from all atoms in the unit cell. This gives the geometrical structure factor S.

Intensity of diffracted beam can be written as $I = F^2 = f^2 S^2$, where S is geometrical structure factor, f is atomic scattering factor and F is diffracted X-ray beam amplitude.

Thus, $F = fS$. The atomic scattering factor (f) is defined as $f = \frac{\text{diffracted amplitude by an atom}}{\text{diffracted amplitude by an electron}}$.

If the atoms are assumed to be points only, then the atomic scattering factor is just equal to the number of electrons present (i.e., the atomic number Z).

Examples: (1) the atomic scattering factor of Na ($Z = 11$) will be larger in comparison to Li ($Z = 3$).

(2) In NaCl, the atomic scattering factors of Na^+ and Cl^- ions are different. The Cl^- ion has more atomic scattering factor.

Thus, the higher scattering factor means higher number of electrons and intensity.

The geometrical structure factor (S) is given by $S = \frac{\text{diffracted amplitude by an unit cell}}{\text{diffracted amplitude by an atom}}$.

Mathematically, $S = \sum_j e^{2\pi i(u_j h + v_j k + w_j l)}$, where (h, k, l) is miller indices of the plane and (u_j, v_j, w_j) is position coordinate of the j^{th} atom.

(1) Simple cubic structure : For simple cubic structure, the effective number of atoms per unit cell is one. Let us take the position coordinate of this atom as origin (0, 0, 0).

Thus, geometrical structure factor $S = \sum e^{2\pi i(u_j h + v_j k + w_j l)} = e^{2\pi i(0h+0k+0l)} = e^0 = 1$

$\Rightarrow \quad S = 1$

The diffracted X-ray beam amplitude becomes $F = fS = f(1) = f$ and intensity of diffracted beam $(I) = f^2$. Hence, all the $(h\,k\,l)$ values are allowed. In other words we can say that all the reflection peaks are allowed in simple cubic structures.

(2) Body centered cubic structures:

For BCC structure, the effective number of atoms per unit cell is equal to 2. We can take the position coordinates of these atoms as (0, 0, 0) and $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$.

Thus, the geometrical structure factor (S) can be given as

$$S = \sum_j e^{2\pi i(u_j h + v_j k + w_j l)} = e^{2\pi i(0h+0k+0l)} + e^{2\pi i\left(\frac{1}{2}h + \frac{1}{2}k + \frac{1}{2}l\right)} = 1 + e^{\pi i(h+k+l)}.$$

For $(h+k+l)$ = even, $S = 1+1 = 2$

For $(h+k+l)$ = odd, $S = 1-1 = 0$

Thus, the amplitude of the diffracted X-ray beam will be given by

$F = 2f$ [For $(h+k+l)$ = even]

$= 0$ [For $(h+k+l)$ = odd]

and the intensity of diffracted beam becomes

$(I) = (2f)^2 = 4f^2$, for $(h+k+l)$ = even

$= 0$, for $(h+k+l)$ = odd

Thus, the reflection peaks (1 1 0), (2 0 0), (2 1 1), (2 2 2),... are allowed for BCC structure and reflection peaks (1 0 0), (1 1 1), (3 0 0),... are absent.

(3) Face centered cubic structure:

For FCC structure, the effective number of atoms per unit cell is equal to 4. Let the position coordinates of these atoms are (0, 0, 0), $\left(\frac{1}{2}, \frac{1}{2}, 0\right)$, $\left(0, \frac{1}{2}, \frac{1}{2}\right)$, $\left(\frac{1}{2}, 0, \frac{1}{2}\right)$.

Thus, the geometrical structure factor (S) can be given as

$$S = \sum_j e^{2\pi i(u_j h + v_j k + w_j l)} = 1 + e^{\pi i(h+k)} + e^{\pi i(k+l)} + e^{\pi i(h+l)}$$

The geometrical structure factor S will be equal to 4 if all the h, k, l are either even or odd and zero otherwise. Thus, the amplitude of the diffracted X-ray beam will be given by

$F = 4f$, h,k,l are either all odd or all even

$= 0$, otherwise

and the intensity of diffracted beam becomes

$I = (4f)^2 = 16f^2$, h,k,l are either all odd or all even

$= 0$, otherwise

Hence, reflection planes (1 1 1), (2 0 0), (2 2 0), (3 1 1),... are allowed (i.e. present) for FCC structure and reflection planes (1 0 0), (1 1 0), (2 1 1),... are not allowed (i.e. absent).

(4) Diamond cubic structure:

For diamond cubic structure, only those reflection peaks will be allowed for which

(i) $(h\,k\,l)$ are all odd, or

(ii) $(h\,k\,l)$ are all even and also $h+k+l=4n$ where $n=1,2,3,...$

i.e. if $(h\,k\,l)$ all are even and $(h+k+l)$ is divisible by 4 then this peak will be present in diamond cubic structure.

(5) Rock salt (NaCl) structure:

The selection rules for NaCl structure is same as FCC structure. There is only one exception. For KCl, the selection rules of NaCl structure is not valid.

SOLVED PROBLEMS

1. Two dimensional lattice has the basis vectors $\vec{a}=2\hat{i};\ \vec{b}=\hat{i}+2\hat{j}$. Find the reciprocal lattice vectors.

Soln. This is a two dimensional problem. If we assume that the third dimensional lattice basis vector $\vec{c}$ is parallel to z-axis i.e. $\vec{c}=\hat{k}$, then we can use the three dimensional relation.

The plane of the reciprocal lattice vector $\vec{A}$ and $\vec{B}$ will be plane of basis vector $\vec{a}$ and $\vec{b}$.

Now, $\vec{A}=\dfrac{(\vec{b}\times\vec{c})}{\vec{a}.(\vec{b}\times\vec{c})}$ and $\vec{B}=\dfrac{(\vec{c}\times\vec{a})}{\vec{b}.(\vec{c}\times\vec{a})}$ $\Rightarrow$ $(\vec{b}\times\vec{c})=(\hat{i}+2\hat{j})\times(\hat{k})=-\hat{j}+2\hat{i}$

$\Rightarrow$ $(\vec{c}\times\vec{a})=(\hat{k})\times(2\hat{i})=2\hat{j}$

$\Rightarrow$ $\vec{a}.(\vec{b}\times\vec{c})=2\hat{i}.(-\hat{j}+2\hat{i})=4$ and $\vec{b}.(\vec{c}\times\vec{a})=(\hat{i}+2\hat{j}).2\hat{j}=4$

$$\vec{A}=\frac{-\hat{j}+2\hat{i}}{4}=\frac{1}{2}\hat{i}-\frac{1}{4}\hat{j} \quad \text{and} \quad \vec{B}=\frac{2\hat{j}}{4}=\frac{1}{2}\hat{j}$$

These are the required reciprocal lattice verctors in two dimensions.

2. The primitive translation vectors of a hexagonal space lattice are

$$\vec{a}=\left(\frac{a}{2}\right)\hat{i}+\left(\frac{1}{16}a\right)\hat{j};\ \vec{b}=-\left(\frac{a}{2}\right)\hat{i}+\left(\frac{1}{16}a\right)\hat{j};\ \vec{c}=c\hat{k}$$

Find (i) volume of the primitive cell and (ii) primitive translations of the reciprocal lattice.

Soln. (i) The volume of the primitive cell is given by

$$V=\left[\vec{a}.(\vec{b}\times\vec{c})\right]$$

Now, $$(\vec{b}\times\vec{c})=\left[-\left(\frac{a}{2}\right)\hat{i}+\left(\frac{1}{16}a\right)\hat{j}\right]\times c\hat{k}=\left(\frac{ac}{2}\right)\hat{j}+\left(\frac{ac}{16}\right)\hat{i}$$

$\Rightarrow$ $$\vec{a}.(\vec{b}\times\vec{c})=\left[\left(\frac{a}{2}\right)\hat{i}+\left(\frac{1}{16}a\right)\hat{j}\right].\left[\left(\frac{ac}{2}\right)\hat{j}+\left(\frac{ac}{16}\right)\hat{i}\right]=\frac{a^2c}{32}+\frac{a^2c}{32}=\frac{a^2c}{16}$$

(ii) Let the primitive translations of reciprocal lattice be $\vec{A}$, $\vec{B}$ and $\vec{C}$, then

$$\vec{A}=2\pi\frac{(\vec{b}\times\vec{c})}{\vec{a}.(\vec{b}\times\vec{c})}$$

Now, $\left(\vec{b}\times\vec{c}\right)=\left[\left(-\frac{a}{2}\right)\hat{i}+\left(\frac{a}{16}\right)\hat{j}\right]\times c\hat{k}=\frac{ac}{2}\hat{j}+\frac{ac}{16}\hat{i}$

Also, $\vec{a}.\left(\vec{b}\times\vec{c}\right)=\frac{a^2c}{16}$

$\Rightarrow$ $\vec{A}=2\pi\left(\frac{\frac{ac}{2}\hat{j}+\frac{ac}{16}\hat{i}}{\frac{a^2c}{16}}\right)=\left(2\frac{\pi}{a}\right)\hat{i}+\left(\frac{16\pi}{a}\right)\hat{j}$

Again, $\vec{B}=\frac{2\pi\left(\vec{c}\times\vec{a}\right)}{\vec{b}.\left(\vec{c}\times\vec{a}\right)}$

Now, $\left(\vec{c}\times\vec{a}\right)=c\hat{k}\times\left[\left(\frac{a}{2}\right)\hat{i}+\left(\frac{a}{16}\hat{j}\right)\right]=\left(\frac{ac}{2}\right)\hat{j}-\left(\frac{ac}{16}\right)\hat{i}$

$\Rightarrow$ $\vec{B}=\left(\frac{2\pi\left(\frac{ac}{2}\right)\hat{j}-\left(\frac{ac}{16}\right)\hat{i}}{\frac{a^2c}{16}}\right)=-\left(\frac{2\pi}{a}\right)\hat{i}+\left(\frac{16\pi}{a}\right)\hat{j}$

Similarly, $\vec{C}=\frac{2\pi\left(\vec{a}\times\vec{b}\right)}{\vec{c}.\left(\vec{a}\times\vec{b}\right)}$

Now, $\left(\vec{a}\times\vec{b}\right)=\left[\left(\frac{a}{2}\right)\hat{i}+\left(\frac{a}{16}\right)\hat{j}\right]\times\left[\left(-\frac{a}{2}\right)\hat{i}+\left(\frac{a}{16}\right)\hat{j}\right]=\left(\frac{a^2}{32}\right)\hat{k}+\left(\frac{a^2}{32}\right)\hat{k}=\frac{a^2}{16}\hat{k}$

$\Rightarrow$ $\vec{C}=\left(\frac{2\pi\frac{a^2}{16}\hat{k}}{\frac{a^2c}{16}}\right)=\left(\frac{2\pi}{c}\right)\hat{k}$

3. The spacing between successive (1 0 0) planes in NaCl is 2.82 Å. X-rays incident on the surface of the crystal is found to give rise to first order Bragg reflection at glancing angle 8.8°. Calculate the wavelength of X-rays.

Soln. According to Bragg's law $2d\sin\theta=n\lambda$.

Here, $d=2.82\text{ Å}=2.82\times10^{-10}\text{ m}, \theta=8.8°$

$\Rightarrow$ $\sin\theta=0.153, n=1$

$\Rightarrow$ $2\times2.82\times10^{-10}\times0.153=\lambda$

$\Rightarrow$ $\lambda=0.863\times10^{-10}\text{ m}=0.863\text{ Å}$

4. Calculate the glancing angle on the plane (110) of a cubic rock salt crystal ($a=2.81$Å) corresponding to second order diffraction maxima of wavelength 0.71 Å.

Soln. Spacing for (110) plane, $d=\frac{a}{\sqrt{1^2+1^2+0}}=\frac{a}{\sqrt{2}}\text{ Å}=\frac{2.81}{\sqrt{2}}=1.987\text{ Å}$

Now. $2d\sin\theta = n\lambda;\ \lambda = 0.71\times10^{-10}$ m; $n = 2$

$$\Rightarrow \quad \sin\theta = \frac{n\lambda}{2d} = \frac{2\times0.71\times10^{-10}}{2\times1.987\times10^{-10}} = 0.3573 \Rightarrow \theta = 20.94\ \text{Å}.$$

5. The molecular weight of rock salt (a simple cubic) crystal is 58.5 kg per kilo-mole and its density is 2.16×10^3 kg/m^3. Taking Avogadro's number $= 6.02\times10^{26}$, calculate the grating space d_{100} of rock salt.
Using this value of lattice constant, calculate the lattice constant, calculate the wavelength of X-rays in second order, if angle of diffraction $\theta = 26°$.

Soln. Mass of one kilo-mole of NaCl = 58.5 kg.
Number of molecules in one kilo-mole = 6.02×10^{26}
Therefore, mass of NaCl crystal = 2.16×10^3 kg/m^3.

$$\text{Volume of one NaCl molecule} = \frac{9.72\times10^{-26}}{2.16\times10^3} = 4.5\times10^{-29}\ \text{m}^3$$

As there are two atoms per NaCl molecule, the volume per atom $= \dfrac{4.5\times10^{-29}}{2} = 2.25\times10^{-29}$ m^3.

If d is the atomic spacing for NaCl crystal, then volume per atom $= d^3$.

$$\Rightarrow \quad d^3 = 2.25\times10^{-29}$$

$$\Rightarrow \quad d = \left(2.25\times10^{-29}\right)^{1/3} = 2.82\times10^{-10}\ \text{m} = 2.82\ \text{Å}$$

$$\Rightarrow \quad d_{100} = 2.82\ \text{Å}$$

According to Bragg's law $2d\sin\theta = n\lambda$

Here, $d = 2.82\times10^{-10}$ m, $\theta = 26° \quad \Rightarrow \sin\theta = 0.4383$

and $n = 2$

$$\Rightarrow \quad 2\lambda = 2\times2.82\times10^{-10}\times0.4383$$

$$\Rightarrow \quad \lambda = 2.82\times0.4383\times10^{-10} = 1.24\times10^{-10}\ \text{m} = 1.24\ \text{Å}$$

6. (a) If X-rays of wavelength 0.5Å are diffracted at an angle of 5° in the first order, what is the spacing between the adjacent planes of the crystal? At what angle will second maximum occur?
(b) The Bragg angle for the first order reflection from (111) plane in a crystal is 60°. Calculate the interatomic spacing if X-rays of wavelength 1.8×10^{-10} m are used.

Soln. (a) According to Bragg's law $2d\sin = n\lambda$

Here, $\lambda = 0.5\ \text{Å} = 0.5\times10^{-10}$ m; $\theta = 5°$

$$\Rightarrow \quad \sin\theta = 0.0871;\ n = 1$$

$$\Rightarrow \quad 2d\times0.871 = 0.5\times10^{-10}$$

$$\Rightarrow \quad d = \frac{0.5\times10^{-10}}{0.1742} = 2.87\times10^{-10}\ \text{m} = 2.87\ \text{Å}$$

For second order maximum, let θ' be the angle of Bragg reflection, then

$$2d\sin\theta' = 2\lambda$$

$$\Rightarrow \quad \sin\theta' = \frac{\lambda}{d} = \frac{0.5\times10^{-10}}{2.87\times10^{-10}} = 0.1742$$

$$\Rightarrow \quad \theta' = 10.03°$$

(b) According to Bragg's law, $2d\sin\theta = n\lambda$

Here, $\theta = 60^\circ \Rightarrow \sin\theta = \sin 60 = 0.866$, $\lambda = 1.8\times10^{-10}$ m; $n = 1$

$\Rightarrow \quad 2d\times0.866 = 1.8\times10^{-10}$

$\Rightarrow \quad d = \dfrac{1.8\times10^{-10}}{1.732} = 1.039\times10^{-10}$ m

This gives us $d_{111} = 1.039\times10^{-10}$ m

If the interatomic spacing for a simple cubic lattice.

$d_{100} = a$, then $d_{111} = \dfrac{a}{\sqrt{3}}$

$\Rightarrow a = d_{100} = d_{111}\times\sqrt{3} = 1.039\times1.732\times10^{-10}$ m $= 1.8\times10^{-10}$ m

7. From the following data calculate the wavelength of neutron beam and its speed. Spacing between successive (100) planes = 3.84 Å; grazing angle 30°; order of Bragg reflection = 1.

Soln. According to Bragg's relation, $2d\sin\theta = n\lambda$

Here, $d = 3.84$ Å $= 3.84\times10^{-10}$ m, $\theta = 30^\circ$; $\sin 30 = \dfrac{1}{2}$; $n = 1$

$\Rightarrow \quad 2\times3.84\times10^{-10}\times\dfrac{1}{2} = 1\times\lambda$

$\Rightarrow \quad \lambda = 3.84\times10^{-10}$ m $= 3.84$ Å

According to de-Broglie relation, $\lambda = \dfrac{h}{p} = \dfrac{h}{mv}$

where h is Planck's constant having a value 6.62×10^{-34} J·s and neutron mass $m = 1.67\times10^{-27}$ kg

$\Rightarrow \quad v = \dfrac{h}{m\lambda} = \dfrac{6.62\times10^{-34}}{1.67\times10^{-27}\times3.84\times10^{-10}} = 1.03\times10^{3}$ ms^{-1}

8. The X-ray powder photograph of a cubic substance taken with Cu K_α radiation $\lambda = 1.54$ Å. Shows diffraction lines at Bragg angle 12.3°, 14.2°, 20.4° and 24.1°. Determine the miller indices of all the lines and size of the cubic unit cell.

Soln. $\because \quad 2d\sin\theta = n\lambda \quad (n=1)$

$d_{hkl} = \dfrac{a}{\sqrt{h^2+k^2+l^2}}$, $\quad \dfrac{2a}{\sqrt{h^2+k^2+l^2}}\sin\theta = \lambda$

$\Rightarrow \dfrac{4a^2\sin^2\theta}{h^2+k^2+l^2} = \lambda^2 \quad \Rightarrow h^2+k^2+l^2 = \dfrac{4a^2}{\lambda^2}\sin^2\theta \quad \Rightarrow \sin^2\theta = \dfrac{\lambda^2}{4a^2}\left(h^2+k^2+l^2\right)$

$\because \sin\theta_1 = \dfrac{\lambda}{2a}\sqrt{h_1^2+k_1^2+l_1^2} \quad \Rightarrow \sin(12.3) = \dfrac{1.54}{2a}\sqrt{3} \quad \Rightarrow a = 6.26$ Å.

$\therefore \left(h_1^2+k_1^2+l_1^2\right):\left(h_2^2+k_2^2+l_2^2\right):\left(h_3^2+k_3^2+l_3^2\right):\left(h_4^2+k_4^2+l_4^2\right)$

$= \sin^2\theta_1 : \sin^2\theta_2 : \sin^2\theta_3 : \sin^2\theta_4$

$= 0.04538 : 0.060 : 0.125 : 0.1667$

$$= 1 : \frac{0.060}{0.04538} : \frac{0.125}{0.04538} : \frac{0.1667}{0.04538}$$

$= 1 : 1.33 : 2.67 : 3.67$

$= 1 : 4/3 : 8/3 : 11/3$

$= 3 : 4 : 8 : 11$

$= (111) \quad (200) \quad (220) \quad (311)$

$\therefore$ system is face centered cubic.

9. The powder diffraction pattern of a BCC crystal is recorded by using Cu K_α radiation of X-rays of wavelength 1.54 Å.

(i) If the (0 0 2) planes diffrated at 60° then lattice parameter a is:

(a) 2.67Å (b) 3.08Å (c) 3.56Å (d) 5.34 Å

(ii) Assuming the atomic mass of constituents atoms to be 50.94 amu the density of the crystal in units of kg/m^3 is:

(a) 3.75×10^3 (b) 4.45×10^3 (c) 5.79×10^3 (d) 8.89×10^3

Soln. (i) $\lambda = 1.54$ Å, $d = \frac{a}{2}$

Angle of diffraction is $2\theta = 60° \Rightarrow \theta = 30°$.

$2d\sin\theta = n\lambda, \quad n = 1$

$\Rightarrow \quad d_{hkl} = \frac{a}{2} \quad \Rightarrow \quad 2\times\frac{a}{2}\sin\theta = \lambda \quad \Rightarrow \quad a\times\frac{1}{2} = 1.54$

$\Rightarrow \quad a = 3.08$ Å

(ii) $M_A = 50.94$ amu

$\frac{n}{a^3} = \frac{N_A\rho}{M_A}$, where, $n = 2$, N_A is Avagadro's number, ρ is mass density and n is number of atoms per unit cell.

$$\therefore \quad \frac{2}{\left(3.08\times10^{-10}\right)^3} = \frac{N_A\rho}{50.94}$$

$$\Rightarrow \quad \rho = \frac{50.94\times2}{\left(3.08\times10^{-10}\right)^3\times6.023\times10^{26}} = 5.79\times10^3 \text{ kg/m}^3.$$

10. A metal with BCC structure shows the first (smallest angle) diffraction peak at a Bragg angle of $\theta = 30°$. The wavelength of X-ray used is 2.1 Å. The volume of the primivitve unit cell of the metal is:

(a) 26.2 Å^3 (b) 13.1 Å^3 (c) 9.3 Å^3 (d) 4.6 Å^3.

Soln. Accordind to Bragg's law, $2d_{hkl}\sin\theta = \lambda$

For first peak (in BCC), $(h\,k\,l) = (110)$

$$2d_{hkl}\times\left(\frac{1}{2}\right) = \lambda \Rightarrow \frac{2}{2}d_{110} = \lambda \Rightarrow \frac{2}{2}.\frac{a}{\sqrt{2}} = \lambda \Rightarrow a = (2.1)\sqrt{2}\text{ Å}$$

Volume of primitive unit cell $= \frac{a^3}{2} = \frac{(2.1)^3 \times \left(\sqrt{2}\right)^3}{2} = 13.1\ \text{Å}^3$

11. The angle of reflection of neutron beam from a crystal of interplanar spacing 3.84 Å is 30°, the speed of neutrons will be

(a) 1.03×10^6 cm/s (b) 1.03×10^5 cm/s (c) 1.03×10^4 cm/s (d) 1.03×10^4 cm/s

Soln. Since, $2d \sin\theta = \lambda \Rightarrow 2 \times 3.84 \sin 30^\circ = \lambda \Rightarrow \lambda = 3.84\ \text{Å} = 3.84 \times 10^{-8}$ cm

Since, $\lambda = \frac{h}{p} = \frac{h}{mv} \Rightarrow v = \frac{h}{m\lambda} = \frac{6.6 \times 10^{-34}}{1.67 \times 10^{-27} \times 2.84 \times 10^{-8}} = 1.03 \times 10^5$ cm/s

12. Zinc crystallises in HCP structure, If r is the radius of zinc atom, the height of the unit cell is

(a) $2r\left(\frac{8}{3}\right)^{1/2}$ (b) $r\left(\frac{8}{3}\right)^{1/2}$ (c) $2r\left(\frac{3}{8}\right)^{1/2}$ (d) $r\left(\frac{3}{8}\right)^{1/2}$

Soln. Since, for HCP structure, $\frac{c}{a} = \sqrt{\frac{8}{3}} \Rightarrow c = \sqrt{\frac{8}{3}}\, a \Rightarrow c = \sqrt{\frac{8}{3}} \cdot 2r$ = height of the unit cell (for HCP structure, $2r = a$).

Hence, correct option is (a).

13. A crystal belongs to a face centered cubic lattice with four atoms in the unit cell. The size of the crystal is 1 cm and unit cell dimension is 1 nm. f is the scattering factor of the atom. **[GATE 2003]**

(A) The number of atoms in the crystal is

(a) 2×10^{21} (b) 4×10^{21} (c) 2×10^{23} (d) 4×10^{24}

(B) The structure factors for (010) and (200) reflection respectively are:

(a) $2f$ and zero (b) zero and $4f$ (c) $2f$ and $2f$ (d) zero and zero

Soln. (A) Unit cell dimension (a) = 1 nm = 1×10^{-9} m and size of the crystal = 1 cm.

$\therefore$ Number of unit cells in the crystal $= \frac{1\text{ cm} \times 1\text{ cm} \times 1\text{ cm}}{10^{-9}\text{ m} \times 10^{-9}\text{ m} \times 10^{-9}\text{ m}} = \frac{10^{-2} \times 10^{-2} \times 10^{-2}\ \text{m}^3}{10^{-9} \times 10^{-9} \times 10^{-9}\ \text{m}^3} = \frac{10^{-6}}{10^{-27}} = 10^{21}$.

$\therefore$ Number of atoms in the crystal = (number of atoms/unit cell) × number of unit cells = 4×10^{21} atoms.

Hence, correct option is (b).

(B) The amplitude of diffracted X-ray beam for fcc lattice having four atoms at $(0, 0, 0)$, $\left(\frac{1}{2}, 0, \frac{1}{2}\right)$, $\left(\frac{1}{2}, \frac{1}{2}, 0\right)$ and $\left(0, \frac{1}{2}, \frac{1}{2}\right)$ positions is given by

$$F = f\left[1 + e^{\pi i(h+l)} + e^{\pi i(h+k)} + e^{\pi i(k+l)}\right] \quad \ldots (i)$$

It is obvious that the amplitude of diffracted X-ray beam is non-zero only if h, k and l are all even or all odd and has a value equal to $4f$. The amplitude of diffracted X-ray beam vanishes for all other odd-even combina-

tions of h. k and l.

Hence, for (010) :

$$F = f\left[1 + e^{\pi i(0+0)} + e^{\pi i(0+1)} + e^{\pi i(1+)}\right] = f\left[1 + e^{0} + e^{\pi i} + e^{\pi i}\right] = f\left[1+1-1-1\right] = 0$$

And for (200): $F = f\left[1 + e^{\pi i(2+0)} + e^{\pi i(0+0)} + e^{\pi i(0+2)}\right] = f\left[1 + e^{2\pi i} + e^{0\cdot\pi i} + e^{2\pi i}\right] = f\left[1+1+1+1\right] = 4f.$

Hence, correct option is (b).

14. Which one of the following statements is not correct about the Brillouin zones (BZ) of a square lattices with constant a? **[GATE 2006]**

(a) The first BZ is a square of side $\left(\frac{2\pi}{a}\right)$ in $k_x - k_y$ plane

(b) The areas of the first BZ and third BZ are the same

(c) The k-points are equivalent in k_x as well as in k_y direction

(d) The area of the second BZ is twice that of the first BZ

Soln. The first BZ is a square of side $\left(\frac{2\pi}{a}\right)$ and second BZ is a square of side $\left(\frac{4\pi}{a}\right)$.

$$\therefore \text{ Area of first BZ} = \left(\frac{2\pi}{a}\right)^2 = \frac{4\pi^2}{a^2} \quad \text{... (i)}$$

$$\text{and area of second BZ} = 4\times\frac{1}{2}\times\left(\frac{2\pi}{a}\right)\cdot\left(\frac{\pi}{a}\right) = \frac{4\pi^2}{a^2} \quad \text{... (ii)}$$

Therefore, area of second BZ = area of first BZ.

Hence, correct option is (d).

15. The primitive translation vectors of the body centered cubic lattice are $\vec{a} = \frac{a}{2}\left(\hat{x} + \hat{y} - \hat{z}\right)$, $\vec{b} = \frac{a}{2}\left(-\hat{x} + \hat{y} + \hat{z}\right)$ and $\vec{c} = \frac{a}{2}\left(\hat{x} - \hat{y} + \hat{z}\right)$. The primitive translation vectors $\vec{A}$, $\vec{B}$ and $\vec{C}$ of the reciprocal lattice are

(a) $\vec{A} = \frac{2\pi}{a}\left(\hat{x} - \hat{y}\right); \vec{B} = \frac{2\pi}{a}\left(\hat{y} + \hat{z}\right); \vec{C} = \frac{2\pi}{a}\left(\hat{x} + \hat{z}\right)$ **[GATE 2008]**

(b) $\vec{A} = \frac{2\pi}{a}\left(\hat{x} - \hat{y}\right); \vec{B} = \frac{2\pi}{a}\left(\hat{y} - \hat{z}\right); \vec{C} = \frac{2\pi}{a}\left(\hat{x} + \hat{z}\right)$

(c) $\vec{A} = \frac{2\pi}{a}\left(\hat{x} + \hat{y}\right); \vec{B} = \frac{2\pi}{a}\left(\hat{y} + \hat{z}\right); \vec{C} = \frac{2\pi}{a}\left(\hat{x} - \hat{z}\right)$

(d) $\vec{A} = \frac{2\pi}{a}\left(\hat{x} + \hat{y}\right); \vec{B} = \frac{2\pi}{a}\left(\hat{y} + \hat{z}\right); \vec{C} = \frac{2\pi}{a}\left(\hat{x} + \hat{z}\right)$

Soln. Volume of the bcc lattice, $V = \vec{a}\cdot\left(\vec{b}\times\vec{c}\right)$

$$= \frac{a}{2}\left(\hat{x} + \hat{y} - \hat{z}\right)\cdot\left[\frac{a}{2}\left(-\hat{x} + \hat{y} + \hat{z}\right)\times\frac{a}{2}\left(\hat{x} - \hat{y} + \hat{z}\right)\right]$$

$$=\left(\frac{a^3}{8}\right)\begin{vmatrix}1 & 1 & -1\\ -1 & 1 & 1\\ 1 & -1 & 1\end{vmatrix}=\frac{a^3}{8}\left[1(1+1)-1(-1-1)-1(1-1)\right]$$

$=4f.$

$$=\frac{a^3}{8}[2+2]=\frac{a^3}{2}$$

es with

i]

∴ Primitive translation vectors of reciprocal lattice are

$$\vec{A}=\frac{2\pi\left(\vec{b}\times\vec{c}\right)}{a\cdot\left(\vec{b}\times\vec{c}\right)}=\frac{2\pi\left[\frac{a}{2}(-\hat{x}+\hat{y}+\hat{z})\times\frac{a}{2}(\hat{x}-\hat{y}+\hat{z})\right]}{\left(\frac{a^3}{2}\right)}$$

$$=\frac{2\pi}{\left(\frac{a^3}{2}\right)}\cdot\left(\frac{a^2}{4}\right)\left[-\hat{x}\times\hat{x}+\hat{x}\times\hat{y}-\hat{x}\times\hat{z}+\hat{y}\times\hat{x}-\hat{y}\times\hat{y}+\hat{y}\times\hat{z}+\hat{z}\times\hat{x}-\hat{z}\times\hat{y}+\hat{z}\times\hat{z}\right]$$

$$=\frac{2\pi}{2a}\left[\hat{z}+\hat{y}-\hat{z}+\hat{x}+\hat{y}+\hat{x}\right]=\frac{\pi}{a}\left[2(\hat{x}+\hat{y})\right]=\frac{2\pi}{a}(\hat{x}+\hat{y})$$

$\hat{y}+\hat{z})$

Similarly, $\vec{B}=\frac{2\pi}{a}(\hat{y}+\hat{z})$ and $\vec{C}=\frac{2\pi}{a}(\hat{z}+\hat{x})$

Hence, correct option is (d).

16. The structure factor of a single cell of identical atoms (form factor f) is given by **[GATE 2008]**

$$S_{hkl}=f\sum_j\exp\left[-i2\pi\left(x_jh+y_jk+z_jl\right)\right]$$

where $\left(x_j, y_j, z_j\right)$ is the coordinate of an atom, and h, k, l are the miller indices. Which one of the following statements is correct for the diffraction peaks of body-centered cubic (bcc) and face-centered cubic (fcc) lattices?

(a) bcc: (200); (110); (222)
fcc: (111); (311); (400)

(b) bcc: (210); (110); (222)
fcc: (111); (311); (400)

8]

(c) bcc: (200); (110); (222)
fcc: (111); (211); (400)

(d) bcc: (200); (210); (222)
fcc: (111); (211); (400)

Soln. **For bcc structure:** (0, 0, 0) and $\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$ are atomic positions

$$\therefore\ S_{hkl}=f\left[1+e^{i\pi(h+k+l)}\right] \qquad \ldots(i)$$

For odd value of $(h+k+l)$ above term will be zero. For, even value of $(h+k+l)$, $S_{hkl}=2f$.

Therefore, for bcc structure, reflections like (100), (111), (210) etc. are missing whereas the diffraction lines corresponding to (110), (200), (222) etc. are present.

For fcc structure: An fcc unit cell has four identical atoms. One of the atoms is contributed by corners and may arbitrarily be assigned coordinates (0, 0, 0), whereas other three are contributed by face-centers and have the coordinates $\left(\frac{1}{2},0,\frac{1}{2}\right)$, $\left(\frac{1}{2},\frac{1}{2},0\right)$ and $\left(0,\frac{1}{2},\frac{1}{2}\right)$.

$$\therefore \quad S_{hkl} = f\left[1 + e^{\pi i(h+l)} + e^{\pi i(h+k)} + e^{\pi i(k+l)}\right] \qquad \text{... (ii)}$$

From above equation (ii), it is clear that structure factor is non-zero only if h, k and l are all even or all odd and has a value equal to 4. Hence reflections of the type (111), (200), (222) etc. are present, whereas those of the type (100), (110), (211) etc. are absent for an fcc crystal.

From the given options : (a) $\left.\begin{matrix}\text{bcc: } (200);\ (110);\ (222)\\ \text{fcc: } (111);\ (3\bar{1}1);\ (400)\end{matrix}\right\}$ is correct.

Hence, correct option is (a).

17. The kinetic energy of a free electron at a corner of the first Brillouin zone of a two dimensional square lattice is larger than that of an electron at the mid point of a side of the zone by a factor b. The value of b is

(a) $b = \sqrt{2}$ (b) $b = 2$ (c) $b = 4$ (d) $b = 8$ **[GATE 2008]**

Soln. The kinetic energy of a free electron at a corner and center of the first Brillouin zone in two-dimensional square lattice is given by

$$\therefore \quad E_{\text{corner}} = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2\right) = \frac{\hbar^2}{2m}\left[\left(\frac{\pi}{a}\right)^2 + \left(\frac{\pi}{a}\right)^2\right] = \frac{\hbar^2}{2m}\left(\frac{2\pi^2}{a^2}\right)$$

$$\text{and} \quad E_{\text{center}} = \frac{\hbar^2}{2m}\left(k_x^2\right) = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 = \frac{\hbar^2}{2m}\left(\frac{\pi^2}{a^2}\right)$$

The ratio of kinetic energies = b

$$\Rightarrow \quad \frac{E_{\text{corner}}}{E_{\text{center}}} = b \quad \Rightarrow \quad \frac{\frac{\hbar^2}{2m}\left(\frac{2\pi^2}{a^2}\right)}{\frac{\hbar^2}{2m}\left(\frac{\pi^2}{a^2}\right)} = b$$

$$\Rightarrow \quad b = 2$$

Hence, correct option is (b).

18. The primitive translation vectors of the face centered cubic (fcc) lattice are **[GATE 2009]**

$$\vec{a}_1 = \frac{a}{2}\left(\hat{j} + \hat{k}\right),\ \vec{a}_2 = \frac{a}{2}\left(\hat{i} + \hat{k}\right),\ \vec{a}_3 = \frac{a}{2}\left(\hat{i} + \hat{j}\right)$$

(A) The primitive translation vectors of the fcc reciprocal lattice are

(a) $\vec{b}_1 = \frac{2\pi}{a}\left(-\hat{i} + \hat{j} + \hat{k}\right);\ \vec{b}_2 = \frac{2\pi}{a}\left(\hat{i} - \hat{j} + \hat{k}\right);\ \vec{b}_3 = \frac{2\pi}{a}\left(\hat{i} + \hat{j} - \hat{k}\right)$

(b) $\vec{b}_1 = \frac{\pi}{a}\left(-\hat{i} + \hat{j} + \hat{k}\right);\ \vec{b}_2 = \frac{\pi}{a}\left(\hat{i} - \hat{j} + \hat{k}\right);\ \vec{b}_3 = \frac{\pi}{a}\left(\hat{i} + \hat{j} - \hat{k}\right)$

(c) $\vec{b}_1 = \frac{\pi}{2a}\left(-\hat{i} + \hat{j} + \hat{k}\right);\ \vec{b}_2 = \frac{\pi}{2a}\left(\hat{i} - \hat{j} + \hat{k}\right);\ \vec{b}_3 = \frac{\pi}{2a}\left(\hat{i} + \hat{j} - \hat{k}\right)$

(d) $\vec{b}_1 = \frac{3\pi}{a}\left(-\hat{i} + \hat{j} + \hat{k}\right);\ \vec{b}_2 = \frac{3\pi}{a}\left(\hat{i} - \hat{j} + \hat{k}\right);\ \vec{b}_3 = \frac{3\pi}{a}\left(\hat{i} + \hat{j} - \hat{k}\right)$

Soln. **(A)** Volume of primitive unit cell of fcc lattice,

$$V=\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)=\frac{a}{2}(\hat{j}+\hat{k})\cdot\left[\frac{a}{2}(\hat{i}+\hat{k})\times\frac{a}{2}(\hat{i}+\hat{j})\right]$$

$$=\begin{vmatrix}0 & a/2 & a/2\\ a/2 & 0 & a/2\\ a/2 & a/2 & 0\end{vmatrix}=0\left(0-\frac{a^2}{4}\right)-\frac{a}{2}\left(0-\frac{a^2}{4}\right)+\frac{a}{2}\left(\frac{a^2}{4}-0\right)$$

$$=\frac{a^3}{8}+\frac{a^3}{8}=\frac{a^3}{4}$$

Therefore, primitive translation vectors of reciprocal lattice are

$$\vec{b}_1=\frac{2\pi(\vec{a}_2\times\vec{a}_3)}{\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)}=\frac{2\pi\left[\frac{a}{2}(\hat{i}+\hat{k})\times\frac{a}{2}(\hat{i}+\hat{j})\right]}{\left(\frac{a^3}{4}\right)}=\frac{2\pi\left(\frac{a^2}{4}\right)}{\left(\frac{a^3}{4}\right)}\left[\hat{i}\times\hat{i}+\hat{i}\times\hat{j}+\hat{k}\times\hat{i}+\hat{k}\times\hat{j}\right]$$

$$=\frac{2\pi}{a}\left[0+(+\hat{k})+(+\hat{j})+(-\hat{i})\right]=\frac{2\pi}{a}(-\hat{i}+\hat{j}+\hat{k})$$

$$\vec{b}_2=\frac{2\pi(\vec{a}_3\times\vec{a}_1)}{\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)}=\frac{2\pi\left[\frac{a}{2}(\hat{i}+\hat{j})\times\frac{a}{2}(\hat{j}+\hat{k})\right]}{\left(\frac{a^3}{4}\right)}=\frac{2\pi\left(\frac{a^2}{4}\right)}{\left(\frac{a^3}{4}\right)}\left[\hat{i}\times\hat{j}+\hat{i}\times\hat{k}+\hat{j}\times\hat{j}+\hat{j}\times\hat{k}\right]$$

$$=\frac{2\pi}{a}(\hat{k}-\hat{j}+\hat{i})=\frac{2\pi}{a}(\hat{i}-\hat{j}+\hat{k})$$

Similarly, $\vec{b}_3=\frac{2\pi}{a}(\hat{i}+\hat{j}-\hat{k})$

Hence, correct option is (a).

(B) The volume of primitive cell of the fcc reciprocal lattice is

(a) $4\left(\frac{2\pi}{a}\right)^3$ (b) $4\left(\frac{\pi}{a}\right)^3$ (c) $4\left(\frac{\pi}{2a}\right)^3$ (d) $4\left(\frac{3\pi}{a}\right)^3$

Soln. **(B)** $V=\vec{b}_1\cdot(\vec{b}_2\times\vec{b}_3)=\frac{2\pi}{a}(-\hat{i}+\hat{j}+\hat{k})\cdot\left[\frac{2\pi}{a}(\hat{i}-\hat{j}+\hat{k})\times\frac{2\pi}{a}(\hat{i}+\hat{j}-\hat{k})\right]$

$$=\left(\frac{2\pi}{a}\right)^3\begin{vmatrix}-1 & 1 & 1\\ 1 & -1 & 1\\ 1 & 1 & -1\end{vmatrix}=\left(\frac{2\pi}{a}\right)^3[-1(1-1)-1(-1-1)+1(1+1)]=\left(\frac{2\pi}{a}\right)^3(2+2)=4\left(\frac{2\pi}{a}\right)^3$$

Hence, correct option is (a).

19. Consider X-ray diffraction from a crystal with a face centered cubic (fcc) lattice. The lattice plane for which there is no diffraction peak is **[GATE 2010]**

(a) (2, 1, 2) (b) (1, 1, 1) (c) (2, 0, 0) (d) (3, 1, 1)

Soln. For fcc lattice, the amplitude of diffracted X-ray beam is given by

$F = f\left[1 + e^{\pi i(h+k)} + e^{\pi i(k-l)} + e^{\pi i(l+h)}\right]$ ... (i)

Soln. For (212), $F = f\left[1 + e^{\pi i(2-1)} + e^{\pi i(1-2)} + e^{\pi i(2-2)}\right] = f(1-1-1+1) = 0$ (i.e., no diffraction)

For (111), $F = f\left[1 + e^{\pi i(1+1)} + e^{\pi i(1+1)} + e^{\pi i(1+1)}\right] = f(1+1+1+1) = 4f$

For (200), $F = f\left[1 + e^{\pi i(2+0)} + e^{\pi i(0+0)} + e^{\pi i(0+2)}\right] = f(1+1+1+1) = 4f$

For (311), $F = f\left[1 + e^{\pi i(3+1)} + e^{\pi i(1+1)} + e^{\pi i(1+3)}\right] = f(1+1+1+1) = 4f$

Hence, correct option is (a).

20. A lattice has the following primitive vectors (in Å), $\vec{a} = 2\left(\hat{j} + \hat{k}\right)$, $\vec{b} = 2\left(\hat{k} + \hat{i}\right)$, $\vec{c} = 2\left(\hat{i} + \hat{j}\right)$. The reciprocal lattice corresponding to the above lattice is **[GATE 2013]**

(a) bcc lattice cube edge of $(\pi/2)$ Å^{-1} (b) bcc lattice with cube edge of (2π) Å^{-1}

(c) fcc lattice with cube edge of $(\pi/2)$ Å^{-1} (d) fcc lattice with cube edge of (2π) Å^{-1}

Soln. Primitive vectors, $\vec{a} = 2\left(\hat{j} + \hat{k}\right)$Å, $\vec{b} = 2\left(\hat{k} + \hat{i}\right)$Å, $\vec{c} = 2\left(\hat{i} + \hat{j}\right)$Å ... (i)

$\therefore$ Volume of unit cell, $V = \vec{a} \cdot \left(\vec{b} \times \vec{c}\right) = \begin{vmatrix} 0 & 2 & 2 \\ 2 & 0 & 2 \\ 2 & 2 & 0 \end{vmatrix} = 0[0-4] - 2[0-4] + 2[4-0] = 8 + 8 = 16\,(\text{Å})^3$.

Now translation vectors of reciprocal lattice

$$\vec{a}^* = \frac{2\pi\left(\vec{b} \times \vec{c}\right)}{\vec{a} \cdot \left(\vec{b} \times \vec{c}\right)} = \frac{2\pi\left[2\left(\hat{k} + \hat{i}\right) \times 2\left(\hat{i} + \hat{j}\right)\right]\text{Å}^2}{16\,\text{Å}^3} = \frac{8\pi}{16}\left[\hat{k} \times \hat{i} + \hat{k} \times \hat{j} + \hat{i} \times \hat{i} + \hat{i} \times \hat{j}\right]\text{Å}^{-1}$$

$$= \frac{\pi}{2}\left[\hat{j} - \hat{i} + \hat{k}\right]\text{Å}^{-1} = \frac{\pi}{2}\left[-\hat{i} + \hat{j} + \hat{k}\right]\text{Å}^{-1}$$

Similarly, $\vec{b}^* = \frac{\pi}{2}\left[\hat{i} - \hat{j} + \hat{k}\right]\text{Å}^{-1}$ ... (ii)

and $\vec{c}^* = \frac{\pi}{2}\left[\hat{i} + \hat{j} - \hat{k}\right]\text{Å}^{-1}$ ... (iii)

$\therefore$ Volume of the reciprocal lattice,

$$V^* = \vec{a}^* \cdot \vec{b}^* \times \vec{c}^* = \frac{\pi}{2}\left(-\hat{i} + \hat{j} + \hat{k}\right) \cdot \left[\frac{\pi}{2}\left(\hat{i} - \hat{j} + \hat{k}\right) \times \frac{\pi}{2}\left(\hat{i} + \hat{j} - \hat{k}\right)\right]$$

$$= \left(\frac{\pi}{2}\right)^3 \begin{vmatrix} -\hat{i} + \hat{j} + \hat{k} \\ \hat{i} - \hat{j} + \hat{k} \\ \hat{i} + \hat{j} - \hat{k} \end{vmatrix} = \frac{\pi^3}{8} \times \left[-1(1-1) - 1(-1-1) + 1(1+1)\right] = \frac{\pi^3}{8} \times [4] = \frac{\pi^3}{8} \times 4 = \frac{\pi^3}{2}$$

which is the volume of primitive unit cell of bcc with cube edge $\left(\pi^3/2\right)$.

Hence, correct option is (a).

21. Neutrons moving with speed 10^3 m/s are used for the determination of crystal structure. If the Bragg angle for the first order diffraction is 30°, the interplanar spacing of the crystal is _____ Å. **[GATE 2014]**

22.

Soln.

23.

Soln

(Given, $m_n = 1.675 \times 10^{-27}$ kg, $h = 6.626 \times 10^{-34}$ J-s)

Soln. Wavelength of neutrons can be given by $\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{1.675 \times 10^{-27} \times 10^{3}}$ m $= 3.96 \times 10^{-10}$ m

$\Rightarrow \lambda = 3.96$ Å

Here, $n = 1$, $\theta = 30°$, $\lambda = 3.96$ Å, $d = ?$

From Bragg's law: $2d \sin\theta = n\lambda$

$\Rightarrow 2 \times d \times \sin 30° = 1 \times 3.96 \times 10^{-10}$

$\Rightarrow 2 \times d \times \frac{1}{2} = 3.96 \times 10^{-10}$

$\Rightarrow d = 3.96 \times 10^{-10} m$

$\Rightarrow d = 3.96$ Å.

Hence, correct answer is (3.96 Å).

22. A beam of X-ray of intensity I_0 is incident normally on a metal sheet of thickness 2 mm. The intensity of the transmitted beam is $0.025\ I_0$. The linear absorption coefficient of the metal sheet (in per m) is _____ (upto one decimal place). **[GATE 2015]**

Soln. Suppose we have a metal sheet of thickness x. If a beam of X-ray of intensity (I_0) is incident on this sheet. The intensity of the transmitted beam can be given by $I = I_0 e^{-\mu x}$ ... (i)

where, μ is absorption coefficient.

According to question, $x = 2$ mm $= 2 \times 10^{-3}$ m
Intensity of incident beam $(I_0) = I_0$
Intensity of transmitted beam $(I) = 0.025\ I_0$ ... (ii)

Putting values of I, I_0 and x from equation (ii) into equation (i), we get, $0.025\ I_0 = I_0 e^{-\mu \times (2 \times 10^{-3})m}$

$\Rightarrow \frac{0.025\ I_0}{I_0} = e^{-\mu \times 2 \times 10^{-3} m} \Rightarrow \frac{25}{1000} = \frac{1}{40} = e^{-(\mu \times 2 \times 10^{-3} m)}$

Taking natural logarithm on both sides, we get

$\Rightarrow -\ell n\ 40 = -\mu \times 2 \times 10^{-3}$ m

$\Rightarrow \mu = \frac{\ell n\ 40}{2 \times 10^{-3}}$ per meter $= \frac{3.69}{2 \times 10^{-3}}$ per meter $= 1.845 \times 10^{3}$ per meter

Hence, correct answer is 1.845×10^3 per meter.

23. A beam of X-rays is incident on a BCC crystal. If the difference between the incident and scattered wave vectors is $\vec{K} = h\hat{x} + k\hat{y} + l\hat{z}$ where $\hat{x}, \hat{y}, \hat{z}$ are the unit vectors of the associated cubic lattice, the necessary condition for the scattered beam to give a Laue maximum is

(a) $h + k + l =$ even (b) $h = k = l$

(c) h, k, l are all distinct (d) $h + k + l =$ odd **[JEST-2012]**

Soln. For BCC crystal, the effective number of atoms is two; one occupies a corner position and the other occupies the center of the cube. If the coordinates of the corner atom be arbitrary taken as (0, 0, 0), then the coordinates

of the other become $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$. Since, both atoms are identical, the diffraction amplitude (F) can be given as

$$F(hkl) = f\sum_j e^{2\pi i(u_j h + v_j k + w_j l)} = f(1 + e^{i\pi(h+k+l)})$$

Above equation gives zero for odd value of $(h + k + l)$ and will give non-zero value for even values of $(h + k + l)$.

Hence, for BCC crystal, the necessary condition for the scattered beam to give a Laue maximum is $h + k + l =$ even.

Hence, correct option is (a).

24. If $\vec{k}$ is the wavevector of incident light $|\vec{k}| = \frac{2\pi}{\lambda}$, λ is the wavelength of light, and $\vec{G}$ is reciprocal lattice vector, then the Bragg's law can be written as

(a) $\vec{k} + \vec{G} = 0$ (b) $2\vec{k} \cdot \vec{G} + G^2 = 0$ (c) $2\vec{k} \cdot \vec{G} + k^2 = 0$ (d) $\vec{k} \cdot \vec{G} = 0$ **[JEST-2016]**

Soln. The Bragg's law in terms of reciprocal lattice vector (G)

$\therefore \quad \vec{k}' = \vec{k} + \vec{G}$

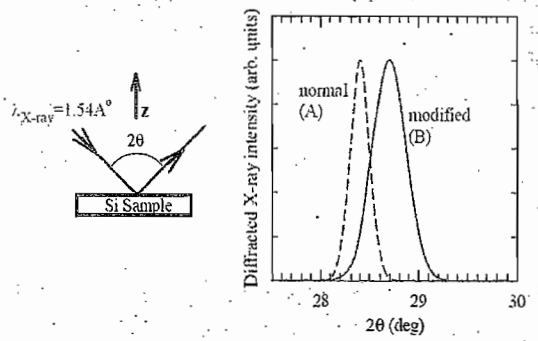
$\Rightarrow \quad \vec{k}' \cdot \vec{k}' = (\vec{k} + \vec{G}) \cdot (\vec{k} + \vec{G}) \Rightarrow |\vec{k}'|^2 = |\vec{k}|^2 + 2\vec{k} \cdot \vec{G} + |\vec{G}|^2$

$\because \quad |\vec{k}'|^2 = |\vec{k}|^2$

$\therefore \quad 2\vec{k} \cdot \vec{G} + G^2 = 0$

Hence, correct option is (b).

25. The figure below shows the Bragg diffraction pattern for X-rays of wavelength 1.54 Å incident on two crystalline silicon thin film samples A and B. The dashed line corresponds to a normal sample A and the continuous line corresponds to another sample B, which is modified due to differences in the growth conditions.



These plots suggest that the modified sample B is

(a) stretched in all directions by 3%

(b) compressed in all directions by 3%

(c) stretched in the z-direction by 1 % and possibly compressed in x and y directions

(d) compressed in the z-direction by 1 % and possibly stretched out in x and y directions

[TIFR-2011]

Soln. From Bragg's law : $2d \sin\theta = n\lambda$

For sample (A), the maximum occurs at 28°24′ and

For sample (B), the maximum occurs at 28°42′.

For modified sample B, the diffracted X-ray intensity peak shifted by 10′ i.e., θ increases. Hence, the distance between planes will decrease in the z-direction.

From Bragg's law $2d \sin\theta = \lambda \Rightarrow \frac{\partial d}{d} + \cot\theta\, \partial\theta = 0$ ($\because \lambda_{X\text{-ray}}$ is fixed)

$$\Rightarrow \frac{\partial d}{d} = -\cot\theta\, d\theta = -(\cot 28°18') \times (18') = -1.857 \times (5.233 \times 10^{-3}) = -9.7 \times 10^{-3}$$

$$\therefore \frac{\partial d}{d}\% = -9.7 \times 10^{-3} \times 100 = -0.97\% \approx 1\%.$$

Therefore, the distance between planes will decrease i.e., the modified sample is compressed in z-direction by 1 %. The sample may be streched out in x and y directions.

Hence, correct option is (d).

26. Metallic copper is known to form cubic crystals and the lattice constant is measured from X-ray diffraction studies to be about 0.36 nm. If the specific is 63.5, one can conclude that

(a) the crystal are of simple cubic type (b) the crystals are of BCC type

(c) the crystals are of FCC type (d) the crystals are a mixture of FCC and BCC types

(e) there is insufficient data to distinguish between the previous options

[TIFR-2012]

Soln. Given, $a = 0.36$ nm

Specific gravity $= \rho = 8.96$ g/cm^3 $= 8{,}96 \times 10^3$ kg/m^3

Avogadro number $(N_A) = 6.023 \times 10^{26}$, $n = ?$

Therefore, from equation

$$\rho = \frac{nM}{N_A a^3} \Rightarrow n = \frac{\rho \cdot N_A \cdot a^3}{M} = \frac{8.96 \times 6.023 \times 10^{26} \times (0.36 \times 10^{-9})^3}{63.3} = 0.0397 \times 10^{29} \times 10^{-27}$$

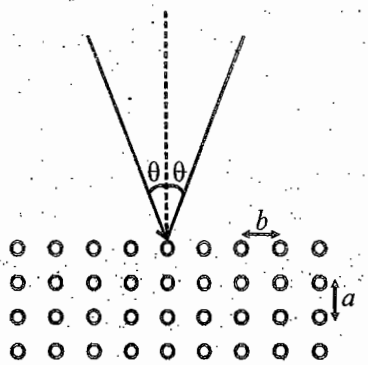
$$= 0.0397 \times 10^2 = 3.97 \cong 4$$

i.e., number of atoms per unit cell = 4.

Hence, the crystals are of FCC type

Hence, correct option is (c).

27. A monochromatic beam of X-rays with wavelength λ is incident at an angle θ on a crystal with lattice spacings a and b as sketched in the figure below.



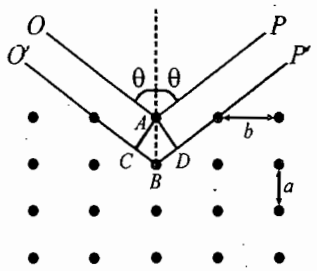
A condition for there to be a maximum in the diffracted X-ray intensity is

(a) $2\sqrt{a^2 + b^2} \sin\theta = \lambda$ (b) $2b \cos\theta = \lambda$

(c) $2a \cos\theta = \lambda$ (d) $(a + b) \sin\theta = \lambda$ **[TIFR-2012]**

Soln. The path difference between OAP and $O'BP' = CB + BD = a\cos\theta + a\cos\theta = 2a\cos\theta$ ... (i)

For maximum intensity, this path difference should be integral multiple of λ.



$\therefore \quad 2a \cos\theta = n\lambda$, where $n = 1, 2, 3, ...$

Hence, correct option is (c).

CAREER ENDEAVOUR

PRACTICE SET

1. In the X-ray diffraction of a set of crystal planes having d equal to 0.18 nm, first order reflection is found to be at an angle of 22°. The wavelength of X-ray is ($\sin 22° = 0.208$)
(a) 0.0749 nm (b) 0.0347 nm (c) 0.749 nm (d) 0.347 nm

2. The angle of diffracted X-rays is 90° from the incident direction of X-rays. The interplanar separation of the planes responsible for the diffraction is given by
(a) $\frac{\lambda}{\sqrt{2}}$ (b) $\frac{\lambda}{2}$ (c) $\sqrt{2}\lambda$ (d) $\frac{\sqrt{3}}{2}\lambda$

3. The diffraction pattern of copper metal was measured with X-ray radiation of wavelength of 1.315 Å. The first order Bragg diffraction peak was found at an angle 2θ of 50.5°. The d-spacing between the diffracting planes in the copper metal is
(a) 3.25 Å (b) 1.54 Å (c) 0.41 Å (d) 4.2 Å

4. The value of θ at which the first order peak in X-ray ($\lambda = 1.53$ Å) diffraction corresponding to (111) plane of a simple cubic structure with the lattice constant, $a = 2.65$ Å, is approximately
(a) 15° (b) 30° (c) 45° (d) 60°

5. Monochromatic X-rays of wavelength 1 Å are incident on a simple cubic crystal. The first order Bragg reflection from (311) plane occurs at an angle of 30° from the plane. The lattice parameter of the crystal in Å is
(a) 1 (b) $\sqrt{3}$ (c) $\sqrt{\frac{11}{2}}$ (d) $\sqrt{11}$

6. An X-ray beam of wavelength 1.54 Å is diffracted from the (110) planes of a solid with a cubic lattice of lattice constant 3.08 Å. The first order diffraction occurs at
(a) $\sin^{-1}\left(\frac{1}{4}\right)$ (b) $\sin^{-1}\left(\frac{1}{2\sqrt{2}}\right)$ (c) $\sin^{-1}\left(\frac{1}{2}\right)$ (d) $\sin^{-1}\left(\frac{1}{\sqrt{2}}\right)$

7. Helium atoms at low temperatures make a perfect closed pack structure of hexagonal lattice with parameters $a = 0.36\ nm$ and $c = 0.59\ nm$. The density of the crystal is approximately
(a) 2000 kg/m^3 (b) 100 kg/m^3 (c) 123 kg/m^3 (d) 200 kg/m^3

8. The compound NaCl has a cubic lattice with density 2.167 g/cm^3. What is the distance between adjacent atoms? Na has molar mass of 23 g/mol, Cl has a molar mass of 35.4 g/mol.

9. Calculate the Bragg angle at which electrons accelerated from rest through a potential difference of 80 V will be diffracted from the (111) planes of an fcc crystal of lattice parameter 3.5 Å.

10. A beam of thermal neutrons emitted from the opening of a reactor is diffracted by the (111) planes of nickel crystal at an angle of 28°30′. Calculate the effective temperature of the neutrons. Nickel has fcc structure and its lattice parameter is 3.52 Å.

ANSWER KEY

1. (a) 2. (b) 3. (b) 4. (b) 5. (d) 6. (b) 7. (d)
8. (5.63Å) 9. (19°41') 10. (169K)

Chapter 3

CRYSTAL BONDING

Crystal Bonding :
The ability to hold the atoms or ions together is called bonding.

Types of bonding:
The individual atoms of a crystalline solid are held together as one system with different types of bonds existing between them. These bonds are classified into five idealised types.

(i) Ionic bonding : Ionic bond is formed by the complete transfer of electron from one atom to another atom.
Example : NaCl. In NaCl, Na has 11 electrons and Cl has 17 electrons. Bond in NaCl crystal is formed by complete transfer of electrons from Na to Cl.

$$\underset{11}{Na} \quad \overset{\curvearrowright}{\underset{17}{Cl}} \longrightarrow Na^{+} - Cl^{-}$$

"Ionic bond is formed between electropositive and electronegative atoms". This bond has spherically symmetric charge distribution. Hence, it is not directional in nature.

(ii) Covalent bonding : Covalent bond is formed by sharing of electrons between two atoms
Examples: H_2, diamond, SiC.

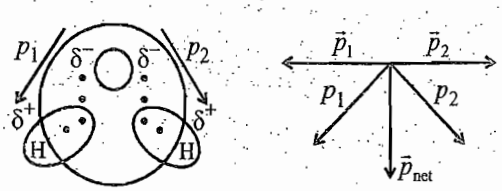
Localized (bound)

In this type of bonding, charge distribution is not spherically symmetric. Charge density is maximum in the direction of bond formation. Hence, this bond is highly directional in nature.

(iii) Metallic bonding : This type of bond is also formed by sharing of electrons but shared electrons pair is not localized. Shared electron pair can move within the solid.
Examples: Cu, Ag, Fe etc.

(iv) Van der Waal bonding : This type of bonding is generally formed between those atoms or molecules which do not have tendency to share or transfer of electrons among them. Van der waal bonding is very weak bonding. This bonding arises due to induced dipole moment. This is slightly directional.
Examples: Inert gases like He, Ne, Ar, solid Argon.

(v) Hydrogen bonding : When a covalent bond is formed between hydrogen atom and highly electronegative atom like oxygen, Cl, etc. then shared electron pair attracted more towards electronegative atoms. This causes the formation of permanent dipole.
Example: H_2O.



Permanent electric dipole moment is the source of H-bonding.

The reason of H-bonding is bond formation between highly electronegative atom and hydrogen. This bond is also directional in nature.

Interatomic forces :

There exists interatomic forces amongst the atoms of crystal that holds the atoms to form crystalline structure. From the very existence of solids, two general conclusions can be drawn.

(i) There must be an attractive force between atoms or molecules in a solid which keeps them together,

(ii) There must also be a repulsive force acting between the atoms. This is why large external pressure is required to compress a solid to any appreciable extent.

When two identical or non-identical atoms, which form a molecule, are brought from infinity to a close proximity, they first attract each other and then, if they are brought closer than a certain distance, repel each other. In other words, a kind of spring effect takes place. As the potential U is related to the force by the relation $F = \frac{-dU}{dr}$, the resulting potential is a function of distance of separation r. The variation of corresponding potential energy U (in eV) with distance r (in Å) is shown in figure.

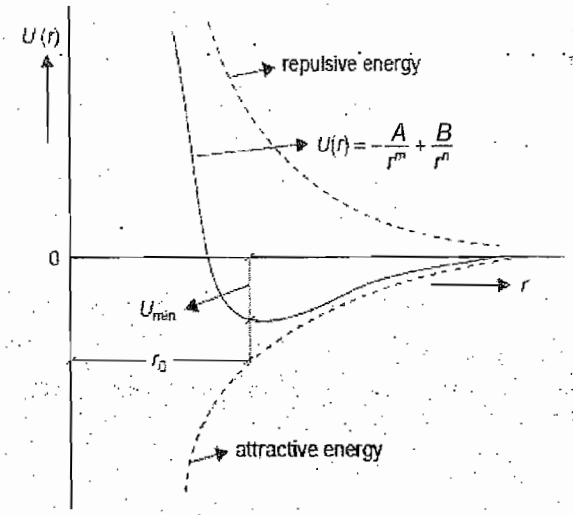
The attractive force gives rise to a negative potential and the repulsive force gives rise to a positive potential shown by dotted curves. The resultant potential enegy is shown by full line curve. It has a minimum at a distance r_0 and represents the equilibrium position, where the attractive and the repulsive forces balance each other and potential energy has a maximum negative value. The potential energy $U(r_0)$ at a distance r_0 is thus responsible for keeping the atoms bound in a solid and gives the cohesive or bonding energy of the solid.

The potential energy $U(r_0)$ is a negative quantity. The positive quantity $-U(r_0) = D$ is called the dissociation energy of the molecule.

The cohesive energy of a solid is defined as the energy which will be given out in the process of the formation of a crystal by bringing neutral atoms from infinity to the position of equilibrium separation.

If the potential energy due to attraction U_a is supposed to vary as the m^{th} power of the distance and that due to repulsion U_r as n^{th} power of r, then

$$U_a \propto \frac{1}{r^m} \Rightarrow U_a = -\frac{A}{r^m} \quad \text{and} \quad U_r \propto \frac{1}{r^n} \Rightarrow U_r = \frac{B}{r^n}$$



Therefore, resultant potential or cohesive energy,

$$U = U_a + U_r = -\frac{A}{r^m} + \frac{B}{r^n}$$

where, A and B are constants of proportionality. The cohesive enegy is generally expressed in eV per atom.

The force between the two atoms is given by

$$F = \frac{-dU}{dr} = \frac{mA}{r^{m-1}} - \frac{nB}{r^{n-1}}$$

At $r = r_0$ the attractive and repulsive forces balance each other and $F(r_0) = 0$. In other words at $r = r_0$, we get

$$\frac{mA}{r_0^{m+1}} - \frac{nB}{r_0^{n+1}} = 0 \qquad \Rightarrow \frac{m}{n} = \frac{B}{A} \cdot r_0^{m-n}$$

$$\Rightarrow \qquad \Rightarrow r_0^{m-n} = \frac{A}{B} \cdot \frac{m}{n} \qquad \text{... (i)}$$

Hence, the potential energy at the equilibrium separation r_0 becomes

$$U(r_0) = \frac{-A}{r_0^m} + \frac{B}{r_0^n} = \frac{-A}{r_0^m}\left(1 - \frac{B}{A} r_0^{m-n}\right) = \frac{-A}{r_0^m}\left(1 - \frac{m}{n}\right)$$

Although the attractive and repulsive forces are in equilibrium at $r = r_0$, the potential energy is not zero as $m \neq n$. If $n >> m$ the total energy is essentially the energy of attraction given by $-\frac{A}{r_0^m}$.

For the potential energy to have a minimum at $r = r_0$ we have $\left.\frac{d^2U}{dr^2}\right|_{r=r_0} > 0$, i.e. it must be positive.

Now, $$\frac{d^2U}{dr^2} = \frac{-m(m+1)A}{r^{m+2}} + \frac{n(n+1)B}{r^{n+2}} > 0$$

Substituting the value of $r = r_0$ from (i), we have

$$-m(m+1)A \cdot \frac{B}{A} \cdot \frac{n}{m}\left(\frac{1}{r_0^{n+2}}\right) + \frac{n(n+1)B}{r_0^{n+2}} > 0$$

$$\Rightarrow \qquad -m - 1 + n + 1 > 0$$

$$\Rightarrow \qquad n - m > 0 \qquad \Rightarrow n > m$$

In other words, a minimum in the energy curve is possible only if $n > m$. Thus the formation of a chemical bond requires that the repulsive forces be of shorter range than the attractive forces.

The energy $U(r_0)$ at the equilibrium distance r_0 is called the binding energy, the energy of cohesion or dissociation energy of the molecule. This much energy is required to separate the atoms of a diatomic molecule to an infinite distance apart.

The cohesive energy may also be defined as the energy released when two atoms are brought close to each other at the equilibrium distance r_0.

Larger the energy released, more stable the bond formed and hence more stable is the crystal structure.

Binding or cohesive energy of ionic crystals:

The calculation of binding or cohesive energy of crystals is one of the major problems of the theory of solids and reuire the knowledge of constituents. For ionic crystals the calculation is simple and in further sections we will describe the calculation of binding energy of NaCl crystal.

The calculation of binding energy of ionic crystal was first given by Born and Madelung and later it was modified by Born and Mayer.

The calculation is based on the assumption that each ionic crystal is composed of positive and negative ions. Each of the ions have a spherical symmetric distribution as in rare gas atoms. Thus, it can be concluded that the force between the ions depends on the distance between the ions ad is independent of the direction of approach. The force between ions is assumed to be electrostatic in nature. Thus the main contribution to the

binding energy arises from electrostatic interaction and is called as Madelung energy.

In ionic crystal there exist two types of interactions, one is long range Coulomb's electrostatic interaction which may be either attractive or repulsive, and the other is short range repulsive interaction.

The coulomb energy of attraction between two ions seperated by a distance r is

$$U_a = -\frac{e^2}{4\pi\varepsilon_0 r} \qquad \ldots(1)$$

In the crystal, each ion interacts with all its neighbouring ions of the same as well as of opposite signs. To take this into account, the net energy of attraction per ion-pair may be written as

$$U_a = \frac{-\alpha e^2}{4\pi\varepsilon_0 r} \qquad \ldots(2)$$

Where, α is the correction factor, called as Madelung constant. For simple crystals α lies between 1.6 and 1.8. For NaCl crystal, $\alpha = 1.7475$ and for CsCl crystal, $\alpha = 1.7626$.

Now, in an ionic crystal as two ions approach each other under coulomb attraction, at a certain distance apart, they begin to repel each other with a force which rise very rapidly with decreae in distance.

$$\therefore \quad U_r = \frac{B}{r^n} \qquad \ldots(3)$$

$$\therefore \quad \text{The total potential energy } U = U_a + U_r = -\alpha\frac{e^2}{4\pi\varepsilon_0 r} + \frac{B}{r^n} \qquad \ldots(4)$$

At equilibrium distance $r = r_0$, U_r will be minimum.

$$\therefore \quad \left.\frac{dU}{dr}\right|_{r=r_0} = 0 = \frac{\alpha^2 e^2}{4\pi\varepsilon_0 r_0^2} - \frac{nB}{r_0^{n+1}}$$

$$\Rightarrow \quad B = \frac{\alpha e^2}{4\pi\varepsilon_0 n} r_0^{n-1}$$

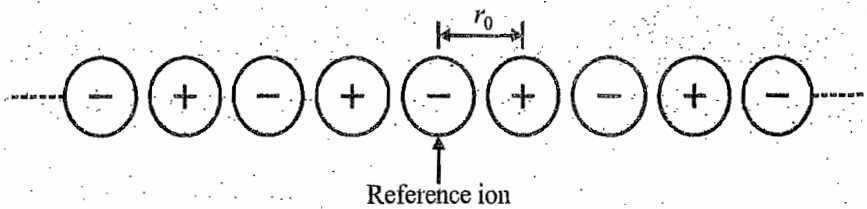
$$\therefore \quad U|_{r=r_0} = -\frac{\alpha e^2}{4\pi\varepsilon_0 r_0} + \frac{\alpha e^2}{4\pi\varepsilon_0 r_0 n} = \frac{-\alpha e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right) \qquad \ldots(5)$$

Madelung constant: Madelung constant is the correction factor in the calculation of lattice energy of an ionic crystal when only nearest neighbours is considered for the calculation of energy.

Madelung constant for one-dimensional chain of ionic crystals:

Consider the simplest case of a one-dimensional crystal consisting of alternate positive and negative ions with interionic distance r_0. The electrostatic energy of the ionic crystal system is given by

$U = E$ = Electrostatic energy due to 1st nearest neighbours
+ Electrostatic energy due to 2nd nearest neighbours
+ Electrostatic energy due to 3rd nearest neighbours
+ – – – – so on.



One-dimensional ionic crystal consisting of alternate positive and negative ions.

For example, in one-dimensional chain of NaCl crystal, each Na^+ ion has two nearest neighbour Cl^- ions at distance r_0, two second nearest neighbour Na^+ ions at distance $2r_0$, two third-nearest neighbour Cl^- ions at distance $3r_0$, so on. Similarly, each Cl^- ion has two nearest neighbour Na^+ ions at distance r_0, two second nearest neighbour Cl^- ions at distance $2r_0$, two third-nearest neighbour Na^+ ions at distance $3r_0$, so on.

Therefore, $$U = E = \frac{-2e^2}{4\pi\varepsilon_0(r_0)} + \frac{-2e^2}{4\pi\varepsilon_0(2r_0)} + \frac{-2e^2}{4\pi\varepsilon_0(3r_0)} + \frac{-2e^2}{4\pi\varepsilon_0(4r_0)} + ---$$

$$= \frac{-2e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5} - ----\right)$$

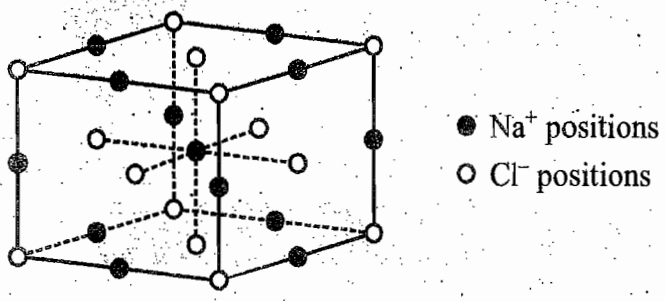
$$= \frac{-2e^2}{4\pi\varepsilon_0 r_0} \cdot [\ln(1+1)] = -\frac{e^2}{4\pi\varepsilon_0 r_0}(2\ln 2) = -\frac{e^2}{4\pi\varepsilon_0 r_0}\alpha$$

Here we have, $\alpha = 2 \ln 2$ = Madelung constant . Hence for one dimensional NaCl crystal the Madelung constant is 2 ln2 or 1.3862.

Madelung constant for three-dimensional chain of ionic crystals:

The calculation of Madelung constant for the three dimensional ionic crystal is not so simple. It is very difficult to write the successive terms by a casual inspection and the series converges slowly. Lets us take example of NaCl crystal. The electrostatic energy of the NaCl crystal system is given by

$U = E$ = Electrostatic energy due to 1st nearest neighbours
+ Electrostatic energy due to 2nd nearest neighbours
+ Electrostatic energy due to 3rd nearest neighbours
+ ---- so on.



Equilibrium positions of ions in sodium chloride crystal

For three dimensional NaCl crystals, each Na^+ ion has 6 nearest neighbour Cl^- ions, 12 second nearest neighbour Na^+ ions, 8 third-nearest neighbours neighbour Cl^- ions, and so on. Similarly, each Cl^- ion has 6 nearest neighbour Na^+ ions, 12 second nearest neighbour Cl^- ions, 8 third-nearest neighbours neighbour Na^+ ions, and so on.

Therefore, $$U = E = \frac{-6e^2}{4\pi\varepsilon_0(r_0)} + \frac{12e^2}{4\pi\varepsilon_0(\sqrt{2}r_0)} + \frac{-8e^2}{4\pi\varepsilon_0(\sqrt{3}r_0)} + \frac{6e^2}{4\pi\varepsilon_0(\sqrt{4}r_0)} + ---$$

$$= \frac{-e^2}{4\pi\varepsilon_0 r_0}\left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \text{-----}\right) = \frac{-\alpha e^2}{4\pi\varepsilon_0 r_0}$$

Here, $\alpha = 6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \text{------} = 1.7475$ is Madelung constant for NaCl crystal.

SOLVED PROBLEMS

1. The energy of two particles in the field of each other at a separation r is given by $U = \frac{\alpha}{r} + \frac{\beta}{r^8}$, where, α and β are constants. At what separation they will form a stable compound?

Soln. The energy of two particles in the field of each other at a separation r is given by $U = \frac{\alpha}{r} + \frac{\beta}{r^8}$.

They will form a stable compound at a separation r_0 such that at that separation the energy U is a minimum, i.e.

$$\left.\frac{dU}{dr}\right|_{r=r_0} = 0 \quad \Rightarrow \quad \frac{dU}{dr} = -\frac{\alpha}{r^2} - \frac{8\beta}{r^9}$$

$$\Rightarrow \quad \left.\frac{dU}{dr}\right|_{r=r_0} = -\frac{\alpha}{r_0^2} - \frac{8\beta}{r_0^9} = 0$$

$$\Rightarrow \quad \frac{\alpha}{r_0^2} + \frac{8\beta}{r_0^9} = 0 \quad \Rightarrow \alpha = \frac{8\beta}{r_0^7}$$

$$\Rightarrow \quad r_0^7 = \frac{8\beta}{\alpha}$$

$$\Rightarrow \quad r_0 = \left(\frac{8\beta}{\alpha}\right)^{1/7}$$

2. The energy of two particles in the field of each other is given by $U = -\frac{\alpha}{r^2} + \frac{\beta}{r^{10}}$, where α and β are constants and r is the separation between the particles. Determine the separation between the particles for a stable compound and also determine the cohesive energy of crystal.

Soln. The energy of the two particles in the field of each other at a separation r is given by

$$U = -\frac{\alpha}{r^2} + \frac{\beta}{r^{10}} \qquad \text{... (i)}$$

They will form a stable compound at a separation r_0 such that at that separation the energy U is minimum i.e.,

$$\left.\frac{dU}{dr}\right|_{r=r_0} = 0 \quad \Rightarrow \quad \frac{dU}{dr} = \frac{2\alpha}{r^3} - \frac{10}{r^{11}} = 0 \quad \Rightarrow r^8 = \frac{5\beta}{\alpha}$$

Therefore, separation for a stable compound $r_0 = \left(\frac{5\beta}{\alpha}\right)^{1/8}$.

Putting the value of $r = r_0$ in equation (i), we have

$$U_{\min} = -\alpha\left(\frac{\alpha}{5\beta}\right)^{1/4} + \beta\left(\frac{\alpha}{5\beta}\right)^{5/4} = \frac{\alpha^{5/4}}{(5\beta)^{1/4}}\left(\frac{\beta}{5\beta} - 1\right) = -\frac{4}{5}\left(\frac{\alpha^{5/4}}{(5\beta)^{1/4}}\right)$$

$$= -\frac{4\alpha}{5}\left(\frac{\alpha}{5\beta}\right)^{1/4} = -\frac{4\alpha}{5r_0^2} = -\frac{4}{5}\left(\frac{\alpha}{r_0^2}\right)$$

Therefore, cohesive energy of the crystal $U_{\min} = -\frac{4}{5}\left(\frac{\alpha}{r_0^2}\right)$.

3. Match the following and choose the correct combination : **[GATE 2005]**

Group-1 (Characteristic)	Group-2 (Element)
P. Atomic configuration $1s^2 2s^2 2p^6 3s^2 3p^6$	1. Na
Q. Strong electropositive	2. Si
R. Strong electronegative	3. Ar
S. Covalent bonding	4. Cl

(a) P-1, Q-2, R-3, S-4 (b) P-3, Q-2, R-4, S-1

(c) P-3, Q-1, R-4, S-2 (d) P-3, Q-4, R-1, S-2

Soln. Since, Argon has 18 atomic number. Therefore, its atomic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6$.
Na is strong electropositive and Cl is strong electronegative. Si is a semiconductor with covalent bonding.
Hence, correct option is (c).

4. The solid phase of an element follows Van der Waals bonding with interatomic potential $V(r) = -\frac{P}{r^6} + \frac{Q}{r^{12}}$, where P and Q are constants. The bond length can be expressed as **[GATE 2007]**

(a) $\left(\frac{2Q}{P}\right)^{1/6}$ (b) $\left(\frac{Q}{P}\right)^{1/6}$ (c) $\left(\frac{P}{2Q}\right)^{1/6}$ (d) $\left(\frac{P}{Q}\right)^{1/6}$

Soln. $V(r) = -\frac{P}{r^6} + \frac{Q}{r^{12}}$,

At $r = r_0$, potential energy will be minimum i.e., $\left.\frac{dV(r)}{dr}\right|_{\text{at } r = r_0} = 0$

$$\Rightarrow \quad -P(-6r_0^{-7}) + Q(-12r_0^{-12-1}) = 0$$

$$\Rightarrow \quad +\frac{6P}{r_0^7} + Q\left(-\frac{12}{r_0^{13}}\right) = 0$$

$$\Rightarrow \quad 6P = \frac{12Q}{r_0^6} \quad \Rightarrow \quad r_0 = \left(\frac{2Q}{P}\right)^{1/6}$$

$\therefore$ Bond length $(r_0) = \left(\frac{2Q}{P}\right)^{1/6}$

Hence, correct option is (a).

5. The total energy of an ionic solid is given by an expression $E = -\frac{\alpha e^2}{4\pi\varepsilon_0 r} + \frac{B}{r^9}$ where α is madelung constant, r is the distance between the nearest neighbours in the crystal and B is a constant. If r_0 is the equilibrium separation between the nearest neighbours then the value of B is **[GATE 2013]**

(a) $\frac{\alpha e^2 r_0^8}{36\pi\varepsilon_0}$ (b) $\frac{\alpha e^2 r_0^8}{4\pi\varepsilon_0}$ (c) $\frac{2\alpha e^2 r_0^{10}}{9\pi\varepsilon_0}$ (d) $\frac{\alpha e^2 r^{10}}{36\pi\varepsilon_0}$

Soln. Total energy, $E = -\frac{\alpha e^2}{4\pi\varepsilon_0 r} + \frac{B}{r^9}$ ... (i)

For equilibrium, $\left.\frac{dE}{dr}\right|_{r=r_0} = 0$, ($r = r_0$ = equilibrium separation)

$$\Rightarrow -\frac{\alpha e^2}{4\pi\varepsilon_0}\left(-\frac{1}{r_0^2}\right) - \left(\frac{9B}{r_0^{10}}\right) = 0 \qquad \Rightarrow \frac{\alpha e^2}{4\pi\varepsilon_0 r_0^2} = \frac{9B}{r_0^{10}}$$

$$\Rightarrow r_0^8 = \frac{(9B)(4\pi\varepsilon_0)}{\alpha e^2} \qquad \Rightarrow B = \frac{\alpha e^2 r_0^8}{36\pi\varepsilon_0}.$$

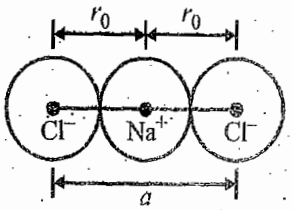
Hence, correct option is (a).

6. The binding energy per molecule of NaCl (lattice parameter is 0.563 nm) is 7.95 eV. The repulsive term of the potential is of the form k/r^9, where k is a constant. The value of madelung constant is _____ (upto three decimal places). **[GATE 2015]**

[electron charge, $e = -1.6\times10^{-19}$ C, $\varepsilon_0 = 8.854\times10^{-12}$ C^2/Nm]

Soln. The cohesive energy of NaCl can be given by :

$$U\big|_{r=r_0} = -\frac{\alpha e^2}{4\pi\varepsilon_0 r_0}\left[1-\frac{1}{n}\right] \quad \text{... (i)} \qquad (\text{For NaCl, } a = 2r_0)$$



$$\Rightarrow 7.95\times1.6\times10^{-19} = -\frac{\alpha\times(1.6\times10^{-19})^2\left[1-\frac{1}{n}\right]}{4\times3.14\times8.854\times10^{-12}\times\left(\frac{a}{2}\right)}$$

$$\Rightarrow 7.95 = -\frac{\alpha\times(1.6\times10^{-19})\times\left[1-\frac{1}{9}\right]}{4\times3.14\times8.854\times10^{-12}\times\left(\frac{0.563}{2}\right)\times10^{-9}} \qquad (\text{Here } n = 9)$$

$$\Rightarrow \alpha = -\frac{9\times7.95\times4\times3.14\times8.854\times0.563\times10^{-21}}{8\times2\times1.6\times10^{-19}}$$

$$\Rightarrow \alpha = -174.98\times10^{-2}$$

$$\Rightarrow \boxed{\alpha = -1.7498}.$$

Hence, correct answer is (α = –1.7498).

PRACTICE SET

1. The potential energy of a diatomic molecule in terms of interatomic distance R is given by

$$U(R) = -\frac{A}{R^m} + \frac{B}{R^n}$$

where A, B, m and n are constants. The equilibrium separation R_e is obtained as

(a) $\left(\frac{nA}{mB}\right)^{\frac{1}{(n-m)}}$ (b) $\left(\frac{nA}{mB}\right)^{\frac{1}{(m-n)}}$ (c) $\left(\frac{nB}{mA}\right)^{\frac{1}{(m-n)}}$ (d) $\left(\frac{nB}{mA}\right)^{\frac{1}{(n-m)}}$

2. The potential energy of a diatomic molecule in terms of interatomic separation R is given by

$$U(R) = -\frac{\alpha}{R^4} + \frac{\beta}{R^{12}}$$

The equilibrium separation is obtained as

(a) $\left(\frac{3\beta}{\alpha}\right)^{1/8}$ (b) $\left(\frac{3\beta}{\alpha}\right)^{1/6}$ (c) $\left(\frac{3\beta}{\alpha}\right)^{1/4}$ (d) $\left(\frac{3\beta}{\alpha}\right)^{1/2}$

3. The Madelung constant A for an infinite linear chain of ions of alternating charge at an equilibrium separation R_e is

(a) 0.3863 (b) 1.3863 (c) 2.3863 (d) 3.3863

4. The potential energy of two particles in stable configuration (at equilibrium) with $m = 2$ and $n = 10$ is equal to

(a) $-\frac{1}{5}\left(\frac{A}{R_e^2}\right)$ (b) $-\frac{2}{5}\left(\frac{A}{R_e^2}\right)$ (c) $-\frac{3}{5}\left(\frac{A}{R_e^2}\right)$ (d) $-\frac{4}{5}\left(\frac{A}{R_e^2}\right)$

5. The Madelung constant for an infinite array of two dimensional ionic charge distribution (i.e. two dimensional NaCl crystal) with equilibrium ion separation as R_e is

(a) 1.6135 (b) 2.6135 (c) 3.6135 (d) 4.6135

6. The potential energy of a diatomic molecule in terms of interatomic distance R is given by

$$U(R) = -\frac{A}{R^m} + \frac{B}{R^n}$$

where A, B, m and n are constants characteristics for the MX-molecules. Attractive and repulsive exponents are related through

(a) $n \ll m$ (b) $n < m$ (c) $n > m$ (d) $n \gg m$

ANSWER KEY

1. (d) 2. (a) 3. (b) 4. (d) 5. (a) 6. (c)

Chapter 4

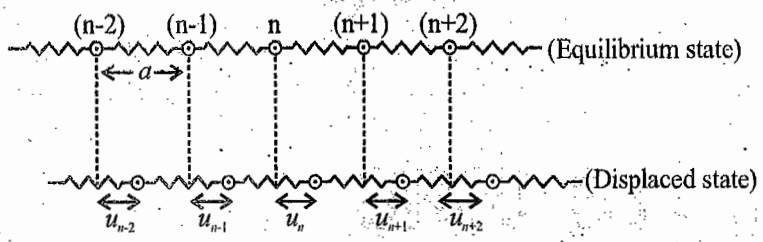
LATTICE VIBRATIONS

Lattice vibration:

A lattice may be regarded as a regular arrangement of atoms in which atoms are joined by elastic massless springs. The motion of any single atom is shared by all the atoms. The lattice can vibrate freely in its normal mode or it may experience forced vibrations. The normal mode vibrations are produced due to its internal energy while forced vibrations produced due to effect of dynamical external forces. The external forces may be of mechanical or electromagnetic type in nature. Normal mode vibrations give informations like thermal properties such as specific heat and thermal conductivity while forced vibrations give informations such as acoustical and optical properties of solids.

Vibrations of one-dimensional monoatomic lattice:

Let us take a one-dimensional chain of atoms of mass m. Let these atoms are attached by massless springs. Let the equilibrium state of the atoms when all the atoms are situated at equally spaced sites represented by ..... $(n-2),(n-1),n,(n+1),(n+2)$.....



In the state of vibration, let the displacement of n^{th} atom, $(n-1)^{th}$ atom, $(n+1)^{th}$ atom, $(n+2)^{th}$ ..... atoms at any instant from mean position are u_n, u_{n-1}, u_{n+1}, u_{n+2}, ... respectively.

If we assume the spring to be perfectly elastic then the force required to produce atomic displacement is defined as follows (Hooke's law).

$$F = Cu \qquad \ldots (1)$$

where u is the displacement of a spring with spring constant C.

Since, the n^{th} atom is attached to $(n-1)^{th}$ and $(n+1)^{th}$ atoms by two springs. Therefore, n^{th} atom experiences two opposite forces which is proportional to the net displacement of the corresponding spring.

The net force on n^{th} atom is given by

$$F = C(u_{n+1} - u_n) - C(u_n - u_{n-1})$$

$$= C(u_{n+1} - 2u_n + u_{n-1}) \qquad \ldots (2)$$

From Newton's law of motion,

$$F = \frac{md^2u_n}{dt^2} \qquad \ldots (3)$$

where, $\frac{d^2u_n}{dt^2}$ is the acceleration of n^{th} atom.

Let the periodic solution of this wave equation as

$$u_n = u_0 \exp i(\omega t - kna) \qquad \ldots (4)$$

where, na represents the x-coordinate of the n^{th} atom in the equilibrium state, $k = \frac{2\pi}{n}$ is the wave vector or propagation vector and ω is the angular frequency of the wave. Similarly, for $(n+1)^{th}$ and $(n-1)^{th}$ atoms, Corresponding expression will be

$$\left.\begin{aligned} u_{n+1} &= u_0 \exp\left[i\{\omega t - k(n+1)a\}\right] \\ u_{n-1} &= u_0 \exp\left[i\{\omega t - k(n-1)a\}\right] \end{aligned}\right\} \qquad \ldots (5)$$

From equations (4) and (5), equation (2) becomes

$$m(-i\omega)^2 u_n = C[e^{ika} + e^{-ika} - 2]u_n \Rightarrow -m\omega^2 = C(2\cos ka - 2)$$

$$\Rightarrow -m\omega^2 = C\left[2\left(1 - 2\sin^2\left(\frac{ka}{2}\right)\right) - 2\right] \Rightarrow +m\omega^2 = +4C\sin^2\left(\frac{ka}{2}\right)$$

$$\Rightarrow \omega^2 = \frac{4C}{m}\sin^2\left(\frac{ka}{2}\right) \Rightarrow \omega = \pm\sqrt{\frac{4C}{m}}\sin\left(\frac{ka}{2}\right)$$

Since the frequency ω will always be positive. Hence,

$$\boxed{\omega = \sqrt{\frac{4C}{m}}\left|\sin\frac{ka}{2}\right|} \qquad \ldots (6)$$

The above equation is called as "the dispersion relation".

Now, we define phase velocity (v_p) and group velocity (v_g). The phase velocity of the waves is defined as the rate of advance of a point of constant phase along the direction of wave propagation and is given by

$$v_p = \frac{\omega}{k} \qquad \ldots (7)$$

The group velocity is defined as the velocity of a group of waves or its envelope and represents the velocity with which the waves transmit energy along the direction of propagation.

Mathematically group velocity is expressed as

$$v_g = \frac{d\omega}{dk} \qquad \ldots (8)$$

For low frequencies, $\omega = \sqrt{\frac{4C}{m}} \sin\left|\frac{ka}{2}\right| = \sqrt{\frac{4C}{m}}\left(\frac{ka}{2}\right)$

$\therefore$ Phase velocity $(v_p) = \frac{\omega}{k} = \sqrt{\frac{4C}{m}} \cdot \left(\frac{a}{2}\right) = a\sqrt{\frac{C}{m}}$

and group velocity $(v_g) = \frac{d\omega}{dk} = \sqrt{\frac{4C}{m}} \cdot \left(\frac{a}{2}\right) = a\sqrt{\frac{C}{m}}$

Thus, the phase velocity and group velocity are same in law frequency range or long wavelength limit.

If s and ρ denote the longitudinal stiffness and the mass per unit length of the line respectively.

$$\rho = \frac{m}{a} \Rightarrow m = \rho a$$

Thus equation (6) becomes

$$\omega = \pm\sqrt{\frac{4s}{\rho a^2}} \sin\left(\frac{ka}{2}\right) = \pm\frac{2}{a}\sqrt{\frac{s}{\rho}} \sin\left(\frac{ka}{2}\right)$$

Let $\sqrt{\frac{s}{\rho}} = v_s$ = a constant for a given lattice and has units of velocity. Here this constant is referred as the velocity of sound waves in solids. Since ω will always be positive, we can write dispersion relation as

$$\omega = \frac{2}{a} v_s \left|\sin\left(\frac{ka}{2}\right)\right|.$$

Limiting cases: (a) At lower frequencies or longer wavelength limit i.e. $\lambda \to \infty \Rightarrow k \to 0$,

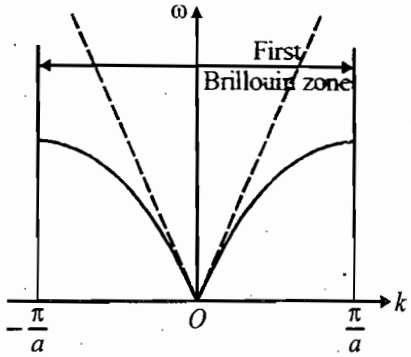
$$\sin\left(\frac{ka}{2}\right) \to \frac{ka}{2}$$

Thus dispersion relation gives, $\omega = 2\sqrt{\frac{C}{m}} \cdot \sin\frac{ka}{2} = 2\sqrt{\frac{C}{m}} \cdot \frac{ka}{2} = a\sqrt{\frac{C}{m}} \cdot k$

The phase velocity $(v_p) = \frac{\omega}{k} = a\sqrt{\frac{C}{m}} = v_s$ and the group velocity $(v_g) = \frac{d\omega}{dk} = a\sqrt{\frac{C}{m}} = v_s$

lower frequencies

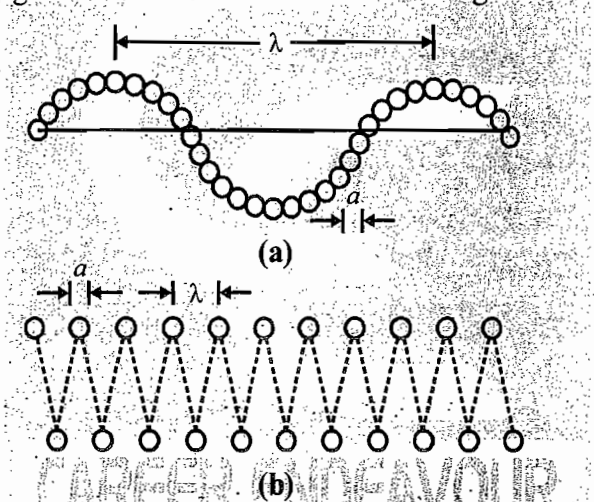
Thus, we can say for monoatomic lattice in the long wavelength limit, phase velocity and group velocity both are same and equal to velocity of sound waves i.e., $v_p = v_g = v_s = a\sqrt{\frac{C}{m}}$



Dispersion relation for a one-dimensional monoatomic lattice

(b) At higher frequencies or smaller wavelength limit, i.e. $\lambda \to 0 \Rightarrow k \to$ higher, thus the phase velocity $\left(v_p\right) = \frac{\omega}{k} = \frac{2}{k}\sqrt{\frac{C}{m}} \sin\frac{ka}{2}$ and group velocity $\left(v_g\right) = a\sqrt{\frac{C}{m}} \cos\frac{ka}{2}$.

Thus, both v_p and v_g are functions of frequency. Thus, for this case, this is called as phenomena of dispersion and the medium is known as dispersive medium. For long wavelength limit, $v_p = v_g = v_s$, i.e. dispersion effects are negligible and medium behaves like a homogeneous continuous medium.



A linear line of atoms consisting a wave (a) Long wavelength case when the motion approaches that of a homogeneous line (b) standing wave

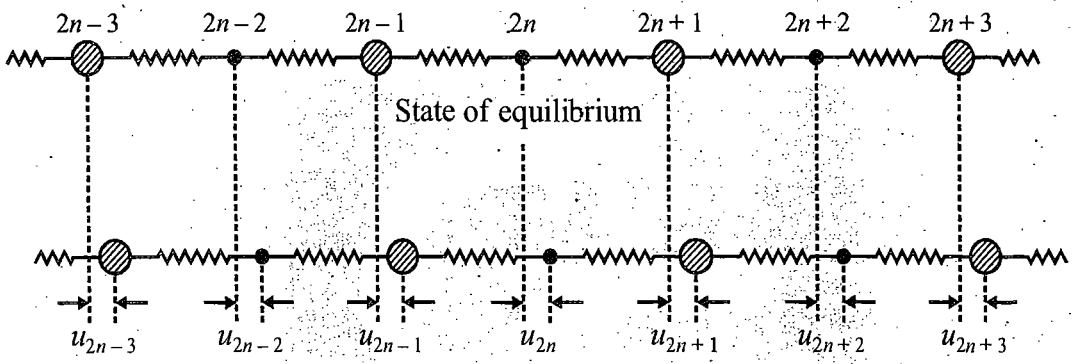
The maximum frequency $\omega = 2\sqrt{\frac{C}{m}}$ will give $k = \frac{\pi}{a}$ or $\lambda = 2a$ and from this, the group velocity $v_g = 0$ and phase velocity $v_p = \frac{2}{k}\sqrt{\frac{C}{m}} = \frac{2a}{\pi}\sqrt{\frac{C}{m}}$.

This confirms that no transfer of signal or energy take place for this frequency limit and the wave behaves like a standing wave.

From above description we can say that only vibration of frequency $\omega < 2\sqrt{\frac{C}{m}} = \frac{2v_s}{a}$ can propagate through the lattice. Hence, the lattice behaves like a low pass filter which transmits only if the frequency lies between zero and $2\sqrt{\frac{C}{m}}$. If we take, typical value of $a \simeq 10^{-10}$ m and sound wave velocity $v_s \cong 10^4$ m/ sec, the maximum frequency which can be transmitted is $\simeq 10^{14}$ Hz.

Vibrations of one-dimensional diatomic lattice.

Let a one-dimensional primitive lattice with basis consists of two atoms of masses m_1 and m_2 $(m_1 < m_2)$ which are placed alternatively along the x-axis with a distance a. In equilibrium state, all the atoms will be located at sites represented by $(2n-2)$, $(2n-1)$, $2n(2n+1)$, $(2n+2)$,.....



State of displacement

Let u_{2n} be the displacement of atom at $2n^{th}$ site during the vibrating motion of atoms.

Thus,

$$\left.\begin{aligned} F_{2n} &= m_1 \frac{d^2u_{2n}}{dt^2} = C\left(u_{2n+1} + u_{2n-1} - 2u_{2n}\right) \\ F_{2n+1} &= m_2 \frac{d^2u_{2n+1}}{dt^2} = C\left(u_{2n+2} + u_{2n} - 2u_{2n+1}\right) \end{aligned}\right\} \quad \ldots \text{(i)}$$

We have the travelling solutions of the type

$u_{2n} = A\exp i(\omega t - 2ka)$ and $u_{2n+1} = B\exp i(\omega t - (2n+1)ka)$

where, k is wavevector.

Now, by writing similar expression for u_{2n-1} and u_{2n+2} and subsituting them in equation (i), we obtain,

$$\left.\begin{aligned} -m_1\omega^2 A &= CB\left(e^{ika} + e^{-ika}\right) - 2CA \\ -m_2\omega^2 B &= CA\left(e^{ika} + e^{-ika}\right) - 2CB \end{aligned}\right\} \quad \ldots \text{(ii)}$$

Since, $\left(e^{ika} + e^{-ika}\right) = 2\cos ka$, then equation (2) gives

$$\left.\begin{aligned} \left(2C - \omega^2 m_1\right)A - \left(2C\cos ka\right)B &= 0 \\ \left(-2C\cos ka\right)A + \left(2C - \omega^2 m_2\right)B &= 0 \end{aligned}\right\} \quad \ldots \text{(iii)}$$

This set of homogeneous linear equations would give rise to non-zero solutions for A and B if

$$\begin{vmatrix} 2C-\omega^2 m_1 & -2C\cos ka \\ -2C\cos ka & 2C-\omega^2 m_2 \end{vmatrix} = 0$$

$$\Rightarrow \quad \omega^4 - \frac{2C(m_1+m_2)}{m_1 m_2}\omega^2 + \frac{4C^2\sin^2 ka}{m_1 m_2} = 0$$

It will give

$$\omega^2 = C\left(\frac{1}{m_1}+\frac{1}{m_2}\right) \pm C\sqrt{\left(\frac{1}{m_1}+\frac{1}{m_2}\right)^2 - \frac{4\sin^2 ka}{m_1 m_2}} \qquad \text{... (iv)}$$

This is the dispersion relation for a linear diatomic lattice.

In monoatomic lattice, there was only one value of ω for one value of wavevector k. But here in diatomic lattice, for one value of k, we have two different values of ω.

Here, plus (+) sign indicates the frequency corresponding to optical branch and minus (–) sign indicates the acoustical branch.

(I) Optical branch : The dispersion relation for optical branch is

$$\omega_+^2 = C\left(\frac{1}{m_1}+\frac{1}{m_2}\right) + C\sqrt{\left(\frac{1}{m_1}+\frac{1}{m_2}\right)^2 - \frac{4\sin^2(ka)}{m_1 m_2}}$$

Limiting cases : (1) At lower frequencies, longer wavelength limit i.e., $\lambda \to \infty \Rightarrow k \to 0,\ \sin(ka) \to ka$.

Thus, $$\omega_+^2 = C\left(\frac{1}{m_1}+\frac{1}{m_2}\right) + C\sqrt{\left(\frac{1}{m_1}+\frac{1}{m_2}\right)^2 - \frac{4(ka)^2}{m_1 m_2}}$$

$$\omega_+^2 = C\left(\frac{1}{m_1}+\frac{1}{m_2}\right) + C\sqrt{\left(\frac{1}{m_1}+\frac{1}{m_2}\right)^2 - \frac{4k^2a^2}{m_1 m_2}}$$

At $k=0,\ \omega_+^2 = C\left(\frac{1}{m_1}+\frac{1}{m_2}\right) + C\left(\frac{1}{m_1}+\frac{1}{m_2}\right) = 2C\left(\frac{1}{m_1}+\frac{1}{m_2}\right) \Rightarrow \omega_+ = \sqrt{2C\left(\frac{1}{m_1}+\frac{1}{m_2}\right)}$

Hence, the value of frequency (ω) is not zero at $k=0$.

(2) At higher frequencies, shorter wavelength limit $\lambda \to 0,\ k \to$ higher, thus $\sin^2(ka) \to 1$

Thus, $\omega_+^2 = C\left(\frac{1}{m_1}+\frac{1}{m_2}\right) + C\sqrt{\left(\frac{1}{m_1}+\frac{1}{m_2}\right)^2 - \frac{4}{m_1 m_2}} = C\left(\frac{1}{m_1}+\frac{1}{m_2}\right) + C\left(\frac{1}{m_1}-\frac{1}{m_2}\right) = \frac{2C}{m_1}$

$$\Rightarrow \quad \omega_+ = \sqrt{\frac{2C}{m_1}}$$

i.e., at $\sin^2(ka) = 1 \Rightarrow \sin ka = \sin\frac{\pi}{2} \Rightarrow k = \frac{\pi}{2a}$ (at the boundary of the first Brillouin zone).

The frequency becomes $\omega = 2\sqrt{\frac{C}{m_1}}$.

(II) Acoustical branch : The dispersion relation for acoustical branch is

$$\omega_-^2 = C\left(\frac{1}{m_1}+\frac{1}{m_2}\right) - C\sqrt{\left(\frac{1}{m_1}+\frac{1}{m_2}\right)^2 - \frac{4\sin^2 ka}{m_1 m_2}}$$

Limiting cases : (1) At low frequencies longer wavelength limit i.e., $\lambda \to \infty \Rightarrow k \to 0$, $\sin(ka) \to ka$.

Thus, $$\omega_-^2 = C\left(\frac{1}{m_1}+\frac{1}{m_2}\right) - C\sqrt{\left(\frac{1}{m_1}+\frac{1}{m_2}\right)^2 - \frac{4k^2a^2}{m_1 m_2}}$$

liatomic

At $k=0$, $\omega_-^2 = C\left(\frac{1}{m_1}+\frac{1}{m_2}\right) - C\left(\frac{1}{m_1}-\frac{1}{m_2}\right) = 0$

ates the

$\Rightarrow \omega_- = 0$

Hence, the value of frequency (ω) is zero at $k=0$.

(2) At higher frequencies, shorter wavelength limit i.e., $\lambda \to 0 \Rightarrow k \to$ higher, thus $\sin^2(ka) \to 1$

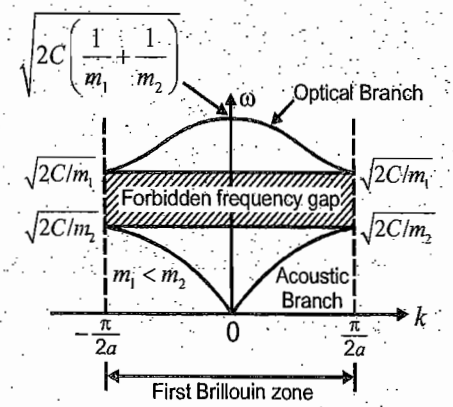
$) \to ka$.

Thus, $\omega_-^2 = C\left(\frac{1}{m_1}+\frac{1}{m_2}\right) - C\sqrt{\left(\frac{1}{m_1}+\frac{1}{m_2}\right)^2 - \frac{4}{m_1 m_2}} = C\left(\frac{1}{m_1}+\frac{1}{m_2}\right) - C\left(\frac{1}{m_1}-\frac{1}{m_2}\right) = \frac{2C}{m_2}$

$\Rightarrow \omega_- = \sqrt{\frac{2C}{m_2}}$

i.e., $\omega_- = \sqrt{\frac{2C}{m_2}}$ for $\sin ka = 1 \Rightarrow \sin ka = \sin\frac{\pi}{2} \Rightarrow k = \frac{\pi}{2a}$

i.e., at the boundary of first Brillouin zone, the frequency of acoustical branch becomes equal to $\sqrt{\frac{2C}{m_2}}$.



Thus, at the zone boundary, the frequency of acoustical branch depend upon the heavier mass (m_2). Therefore, frequency of optical branch and acoustical branch are different at zone boundary. The difference in the frequencies is known as forbidden frequency gap.

Phonons:

Since we know that the energy of a electromagnetic wave is quantized and the quantum of energy is known as photon. In the similar way, the energy of a lattice vibration of an elastic wave is also quantized and the quantum of lattice vibration is called as phonon. All types of lattice vibrations in crytals comprise phonons such as thermal vibrations are thermally excited phonons, sound waves are acoustical phonons and excitations of the branch generate optical phonons.

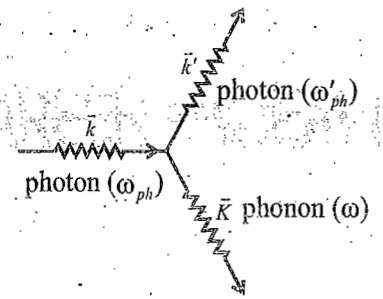
The energy of phonon is given by $\hbar\omega$, where ω is the angular frequency of a mode of vibration.

If n is the number of phonons in a particular mode of vibration, the total energy of that mode is $n\hbar\omega$, where n can be zero or a positive integer.

Momentum of phonons: Physically, a lattice phonon does not carry any momentum, but it interacts with other particles and fields as if it has a momentum $\hbar\vec{K}$, where $\vec{K}$ represents the wavevector of the phonon. Also from the de-Broglie relation $p = \frac{h}{\lambda} = \hbar\vec{K}$.

Thus, it is apparent that a phonon of wavelength λ carries a momentum $\hbar\vec{K}$. This momentum is also called as crystal momentum.

The wavevector conservation law for elastic scattering or the Bragg's diffraction of X-ray photons from crystal is given by $\vec{k}' = \vec{k} + \vec{G}$, where $\vec{k}'$ and $\vec{k}$ represent the wavevectors for the scattered and incident photons respectively and $\vec{G}$ is the reciprocal lattice vector. The conservation of momentum and energy gives $\hbar\vec{k}' = \hbar\vec{k} + \hbar\vec{G}$ and $\hbar\omega_{ph} = \hbar\omega'_{ph}$ such a process in which the frequency of the incident photon is the same as that of the scattered photon is called **normal or N-process.**



Inelastic scattering of incident photon to produce scattered photon alongwith the emission of a phonon.

In case of inelastic scattering, the wavevector conservation law is given by $\vec{k}' + \vec{K} = \vec{k} + \vec{G}$.

Accordingly, the conservation momentum and energy gives $\hbar\vec{k}' + \hbar\vec{K} = \hbar\vec{k} + \vec{G}$ and $\hbar\omega'_{ph} + \hbar\omega = \hbar\omega_{ph}$, where ω is the such a process is called **umclapp or U-process.**

Phonon do not interact with each other i.e. phonon-phonon scattering does not occur.

SOLVED PROBLEMS

1. In a cubic system with cell edge a, two phonons with wave vectors $\vec{q}_1$ and $\vec{q}_2$ collide and produce a third phonon with a wave vector $\vec{q}_3$ such that $\vec{q}_1 + \vec{q}_2 = \vec{q}_3 + \vec{R}$, where, $\vec{R}$ is a lattice vector. Such a collision process will lead to **[GATE 2002]**

(a) finite thermal resistance. (b) zero thermal resistance.

(c) an infinite thermal resistance. (d) a finite thermal resistance for certain $|\vec{R}|$ only.

Soln. In $\vec{q}_1 + \vec{q}_2 = \vec{q}_3 + \vec{R}$, the phonon $\vec{q}_3$ destroys momentum $\hbar\vec{R}$. So conservation of momentum does not hold. Therefore, a finite value of thermal resistance comes out.
Hence, correct option is (a).

2. A cubic cell consists of two atoms of masses m_1 and m_2 $(m_1 > m_2)$ with m_1 and m_2 atoms situated on alternate planes. Assuming only nearest neighbours interactions, the center of mass of the two atoms.

(a) moves with the atoms in the optical mode and remains fixed in the acoustic mode **[GATE 2003]**
(b) remains fixed in the optical mode and moves with the atoms in the acoustic mode
(c) remains fixed in both optical and acoustic modes
(d) moves with the atoms in both optical and acoustical

Soln. **For optical brands :** $\frac{A}{B} = -\frac{m_1}{m_2}$. This indicates that the two atoms move in opposite directions and their amplitudes are inversely proportional to their masses so that the center of mass of the unit cell remains unchanged.

For acoustical branch : $\frac{A}{B} = +1$. This means that the two atoms of different masses move in the same direction with the same amplitude and there is a movement of their centers of masses as well.
Hence, correct option is (b).

3. The number of independent elastic constant in an isotropic cubic solid is **[GATE 2003]**

(a) 1 (b) 2 (c) 3 (d) 4

Soln. There are three elastic constant ε_{XX}, ε_{YY} and ε_{ZZ} which are independent for isotropic solid (cubic).
Hence, correct option is (c).

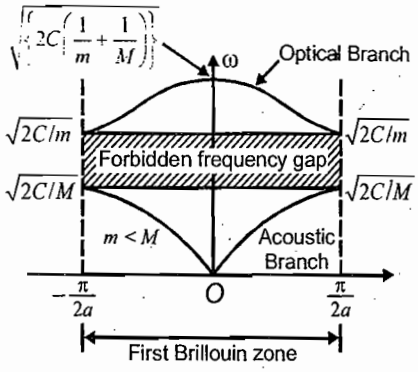
4. A linear diatomic lattice of lattice constant a with masses M as m, $(M > m)$ are coupled by a force constant C. The dispersion relation is given by **[GATE 2008]**

$$\omega_{\pm}^2 = C\left(\frac{M+m}{Mm}\right) \pm \left[C^2\left(\frac{M+m}{Mm}\right)^2 - \frac{4C^2}{Mm}\sin^2\frac{ka}{2}\right]^{1/2}$$

Which one of the following statement is incorrect ?

(a) The atoms vibrating in transverse mode correspond to the optical branch.
(b) The maximum frequency of the acoustic branch depends on the mass of the lighter mass m.
(c) The dispersion of frequency in the optical branch is smaller than in the acoustic branch.
(d) No normal modes exist in the acoustic branch for any frequency greater than the maximum frequency at $k = \frac{\pi}{a}$.

Soln.



Dispersion curves for linear diatomic lattice showing acoustical and optical modes.

From above figure, it is clear that ω_{optical} is larger than $\omega_{\text{acoustical}}$.

Hence, correct option is (c).

5. In a cubic crystal, atoms of mass M_1 lie on one set of planes and atoms of mass M_2 lies on planes interleaved between these of the first set. If C is the force constant between nearest neighbour planes, the frequency of lattice vibrations for the optical phonon branch with wave vector $k = 0$ is **[GATE 2009]**

(a) $\sqrt{2C\left(\frac{1}{M_1}+\frac{1}{M_2}\right)}$ (b) $\sqrt{C\left(\frac{1}{2M_1}+\frac{1}{M_2}\right)}$

(c) $\sqrt{C\left(\frac{1}{M_1}+\frac{1}{2M_2}\right)}$ (d) zero

Soln. For optical phonon branch, frequency of lattice vibration is given by $\omega = \sqrt{2C\left(\frac{1}{M_1}+\frac{1}{M_2}\right)}$.

Hence, correct option is (a).

6. For a three-dimensional crystal having N primitive unit cells with a basis of p atoms, the number of optical branch is **[GATE 2011]**

(a) 3 (b) $3p$ (c) $(3p-3)$ (d) $3N-3p$

Soln. For a $3D$ crystal, number of optical branches = $(3p-3)$

Hence, correct option is (c).

7. The dispersion relation for a one-dimensional monatomic crystal with lattice spacing a, which interacts via nearest neighbour harmonic potential, is given by $\omega = A\left|\sin\frac{ka}{2}\right|$ where, A is a constant of appropriate unit.

(A) The group velocity at the boundary of first Brillouin zone is **[GATE 2012]**

(a) zero (b) 1 (c) $\sqrt{\frac{Aa^2}{2}}$ (d) $\frac{1}{2}\sqrt{\frac{Aa^2}{2}}$

(B) The force constant between the nearest neighbour of the lattice is (M is the mass of the atom)

(a) $\frac{MA^2}{4}$ (b) $\frac{MA^2}{2}$ (c) MA^2 (d) $2MA^2$

Soln. **(A)** $\omega = A\left|\sin\frac{ka}{2}\right|$ ... (i)

At the boundary of first Brillouin zone, i.e. at $k = \pm\frac{\pi}{a}$, equation (i) gives

$$\omega = A\left|\sin\left(\pm\frac{\pi}{a}\cdot\frac{a}{2}\right)\right| = A\left|\sin\left(\pm\frac{\pi}{2}\right)\right| = A \quad \text{... (ii)}$$

$\therefore$ Group velocity $(v_g) = \frac{d\omega}{dk} = 0$

$\therefore$ Group velocity at the boundary of first Brillouin zone is zero.

It can also be solved as : Group velocity $v_g = \frac{d\omega}{dk} = \frac{d}{dk}A\left|\sin\frac{ka}{2}\right| = \frac{Aa}{2}\left|\cos\frac{ka}{2}\right|$ ... (iii)

At the boundary of first Brillouin zone i.e. for $k = \pm\frac{\pi}{a}$, equation (ii) gives

$$\Rightarrow \quad v_g = \frac{Aa}{2}\cos\left(\frac{\pi}{2}\right) \quad \Rightarrow \quad v_g = 0.$$

Hence, correct option is (a).

(B) The dispersion relation (ω versus k) for one-dimensional monatomic lattice is given by

$$\omega = \sqrt{\frac{4C}{M}}\left|\sin\frac{ka}{2}\right| \quad \text{... (iv)}$$

Comparing equation (iv) and equation (i), we get (where, C is force constant)

$$A = \sqrt{\frac{4C}{M}} \quad \Rightarrow \quad A^2 = \frac{4C}{M} \quad \Rightarrow \quad C = \frac{MA^2}{4}.$$

Hence, correct option is (a).

8. Group-I contains elementary excitations in solids. Group-II gives the associated fields with these excitations. Match the excitations with their associated field and select your answer as per codes given below. **[GATE 2013]**

Group-I	Group-II
P. Phonon	i. photon + lattice vibration
Q. Plasmon	ii. electron + elastic deformation
R. Polaron	iii. collective electron oscillations
S. Polarition	iv. elastic wave

Codes:

(a) P-iv, Q-iii, R-i, S-ii (b) P-iv, Q-iii, R-ii, S-i

(c) P-i, Q-iii, R-ii, S-iv (d) P-iii, Q-iv, R-ii, S-i

Soln.

Group-I	Group-II
P. Phonon	iv. elastic wave
Q. Plasmon	iii. collective electron oscillations
R. Polaron	ii. electron + elastic deformation
S. Polarition	i. photon + lattice vibration

Hence, correct option is (b).

9. The dispersion relation for phonons in a one dimensional monatomic Bravais lattice with lattice spacing a and consist of ions of masses M is given by **[GATE 2015]**

$$\omega(k) = \sqrt{\frac{2C}{M}\left[1 - \cos(ka)\right]}$$

where, ω is the frequency of oscillation, k is the wave vector and C is the spring constant. For the long wavelength modes $(\lambda \gg a)$, the ratio of the phase velocity to the group velocity is_____.

Soln. The $\omega - k$ relation for monatomic lattice is given by

$$\omega(k) = \sqrt{\frac{2C}{M}\left[1 - \cos(ka)\right]} \quad \text{... (i)}$$

$$\Rightarrow \quad \omega(k) = \sqrt{\frac{2C}{M}\left[1 - \left\{1 - 2\sin^2\left(\frac{ka}{2}\right)\right\}\right]} \quad \text{... (ii)}$$

$$\Rightarrow \quad \omega(k) = \sqrt{\frac{2C}{M}\left[1 - 1 + 2\sin^2\left(\frac{ka}{2}\right)\right]}$$

$$\Rightarrow \quad \omega(k) = \sqrt{\frac{4C}{M}} \cdot \left|\sin\frac{ka}{2}\right| \quad \text{... (iii)}$$

Here, we have taken modulus of $\sin\frac{ka}{2}$ because $\omega(k)$ cannot be negative.

For long wavelength modes $(\lambda \gg a)$, i.e., $k = \left(\frac{2\pi}{\lambda}\right) \to 0 \Rightarrow \sin\left(\frac{ka}{2}\right) \to \frac{ka}{2}$

$\therefore$ equation (iii) $\Rightarrow \quad \omega(k) = \sqrt{\frac{4C}{M}}\left[\frac{ka}{2}\right]$ ... (iv)

$\therefore$ Phase velocity, $(v_p) = \frac{\omega}{k} = \sqrt{\frac{4C}{M}} \cdot \left(\frac{a}{2}\right)$ ... (v)

and group velocity, $(v_g) = \frac{d\omega}{dk} = \sqrt{\frac{4C}{M}} \cdot \left(\frac{a}{2}\right)$ ... (vi)

$\therefore$ Ratio of phase velocity to the group velocity

$$\Rightarrow \quad \frac{v_p}{v_g} = \frac{\sqrt{\frac{4C}{M}} \cdot \left(\frac{a}{2}\right)}{\sqrt{\frac{4C}{M}} \cdot \left(\frac{a}{2}\right)} = 1$$

Hence, correct answer is (1).

No. of branches in a solid:-

If there are p atoms in the primitive unit cell

No. of branches	1D	2D	3D
no. of branches	p	2p	3p
Optical	p-1	2p-2	3p-3
Acoustical	1	2	3

From Ugc

PRACTICE SET

1. The natural cut-off frequency ω_m for a one dimensional periodic lattice with force contant K and mass M is given by

(a) $\frac{4K}{M}$ (b) $\frac{4M}{K}$ (c) $\left(\frac{4K}{M}\right)^{1/2}$ (d) $\left(\frac{4M}{K}\right)^{1/2}$

2. The visible light of wavelength 4000Å undergoes scattering from a diamond crystal of refractive index 2.42. Calculate the maximum frequency of the phonon generated and the fractional change in the frequency of the incident radiation, given the velocity of sound in diamond as 1.2×10^4 ms^{-1}.

3. Compute the cut-off frequency for a linear monoatomic lattice if the velocity of sound and the interatomic spacing in the lattice are $3\times10^3\ ms^{-1}$ and $3\times10^{-10}\ m$ respectively.

4. The dispersion relation for a one-dimensional monoatomic crystal with lattice spacing a, which interacts via nearest neighbour harmonic potential, is given by $\omega = A\left|\sin\frac{ka}{2}\right|$ where, A is a constant of appropriate unit. The group velocity at the boundary of first Brillouin zone is

(a) zero (b) 1 (c) $\sqrt{\frac{Aa^2}{2}}$ (d) $\frac{1}{2}\sqrt{\frac{Aa^2}{2}}$

5. The dispersion relation for phonons in a one dimensional monatomic Bravais lattice with lattice spacing a and consist of ions of masses M is given by

$$\omega(k) = \sqrt{\frac{2C}{M}\left[1-\cos(ka)\right]}$$

where, ω is the frequency of oscillation, k is the wave vector and C is the spring constant. For the long wavelength modes $(\lambda \gg a)$, the ratio of the phase velocity to the group velocity is

(a) zero (b) 1 (c) 2 (d) 3

6. For one dimensional monoatomic lattice ω and k relation is given by $\omega = A\sin\left(\frac{ka}{2}\right)$. What is spring constant of the vibration, if the mass of atoms are M.

$\omega = A\sin\left|\frac{ka}{2}\right|$ $\omega = \sqrt{\frac{4C}{M}}\sin\left|\frac{ka}{2}\right|$ $\omega = \sqrt{\frac{4C}{M}}\sin\left|\frac{ka}{2}\right|$

$\Rightarrow A = \sqrt{\frac{4C}{M}}$ $A^2 = \frac{4C}{M}$ $\Rightarrow C = \frac{MA^2}{4}$

$A^2 = \frac{4C}{M}$ $\Rightarrow \left(\frac{MA^2}{4}\right) = C$

ANSWER KEY

1. (c) **2. (9.12×10^{11}, 1.9×10^{-4})** **3. (2×10^{13} Hz)** **4. (a)** **5. (b)**

6. $\left(\frac{MA^2}{4}\right)$

Chapter 5

THERMAL PROPERTIES OF MATERIALS

The specific heat of solid:

From elementary knowledge, we know that the specific heat is the amount of heat energy that must be supplied to a mole of solid to raise its temperature by one degree. So, when some heat energy is supplied to a solid, its temperature rises and its internal energy is increased. The increase in the internal energy is manifested mainly as (i) an increase in the vibration of atoms about their mean position and (ii) an increase in the kinetic energy of free electrons. The corresponding specific heats are known as the lattice specific heat and the electronic specific heat, respectively. In order to measure the specific heat, either the volume or the pressure must be kept constant. In general, it is measured at constant volume, ie.

$$C_V = \left(\frac{dE}{dT}\right)_V \qquad \ldots (1)$$

where E is the internal energy and T is the temperature of the system.

The classical model (Dulong-Petit's law):

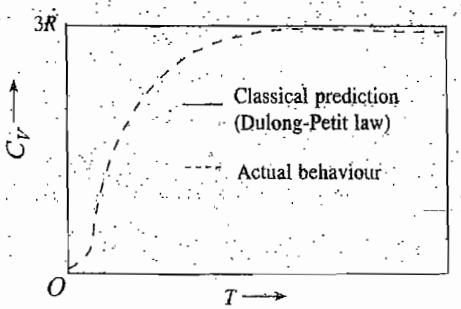
From the kinetic theory of gases, we know that the kinetic energy of an atom of a monoatomic gas at temperature T is $(3/2)\,k_B T$, where k_B is the Boltzmann constant. Since an atom has three degrees of (translational) freedom, therefore, the energy $(1/2)\,k_B T$, is associated with each degree of freedom of the atom. Also, to each translational degree of freedom, there are associated two additional degrees of freedom, because energy can appear as kinetic or potential. If there are N atoms ($= N_A$, Avogadro's number for a monoatomic solid) in a mole of the solid, the total internal energy is

$$3 \times 2 \times N \times \frac{1}{2} k_B T = 3Nk_B T = 3RT \qquad \ldots (2)$$

where $Nk_B = R$, the universal gas constant. Therefore, the specific heat at constant volume is

$$C_V = \left(\frac{dE}{dT}\right)_V = 3R = 5.96 \text{ cal} \cdot \text{mol}^{-1}\,\text{K}^{-1}$$

This is known as Dulong-Petit's law and is found to be generally correct at room temperature and above, for elements of atomic weight greater than 40. However, the following experimental facts suggest that the above law fails under other conditions, viz.



Specific heat of a solid
at low temperature

1. At low temperatures, the specific heat of all elemental solids is found to approach zero as T^3 in insulators and as T in metals. In superconductors, the drop is even faster.
2. In magnetic solids, there is a large contribution to the specific heat near the temperature at which the manetic moments become ordered.
3. A number of low atomic number and high melting point elements (e.g. B, Be, C and Si) show lower specific heats than predicted by Dulong-Petit's law.
4. A number of electropositive metals (e.g. Na, Cs, Ca and Mg) show an increase of specific heat above the maximum value $3R$ with an increase of temperature.

The Einstein model:

Einstein was the first person to resolve the problem of specific heat of solids by the application of Planck's quantum theory. He assumed that a crystalline solid made up of N atoms (per mole) could be regarded as an array of atomic oscillators vibrating in three independent directions (as assumed for the classical calculations) with a constant frequency ν and that the allowed energy states of oscillators are integral multiples by $h\nu$.

It may be shown that a crystal containing N atoms which interact according to Hooke's law is mechanically equivalent to a set of $3N$ independent oscillators. Thus, the total internal energy of the crystal is equal to the sum of the mean energies of the individual oscillators. Accordingly, each of the $3N$ harmonic oscillators will have quantised energies.

$$\varepsilon_n = n\hbar\omega = nh\nu \qquad \ldots (4)$$

when the quantum number $n = 0, 1, 2, 3, \ldots\ldots$, $\hbar = h/2\pi$ and $\omega = 2\pi\nu$. Here the 'zero point energy' $(h\nu/2)$ is neglected as it will not affect the result.

The number of oscillators N_n of each energy state is determined from the Boltzmann function as

$$N_n = N_0 \exp\left(-\frac{\varepsilon_n}{k_B T}\right) = N_0 \exp\left(-\frac{nh\nu}{k_B T}\right) \qquad \ldots (5)$$

where N_0 is the number of oscillators in the zero energy state. Further, the average vibrational energy of an oscillator is given by

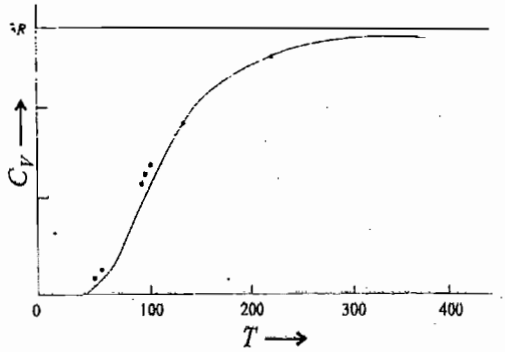
$$\bar{\varepsilon} = \frac{\varepsilon}{N} = \frac{\sum_n N_n \varepsilon_n}{\sum_n N_n} = \frac{h\nu}{\exp\left(\frac{h\nu}{k_B T}\right) - 1} \qquad \ldots (6)$$

Taking into account the three independent harmonic oscillators (N atoms and 3 independent directions), the total internal energy is given by

$$E = \frac{3Nh\nu}{\exp\left(\frac{h\nu}{k_B T}\right) - 1} \qquad \ldots (7)$$

and the specific heat

$$C_V = \left(\frac{dE}{dt}\right)_V = 3Nk_B \left(\frac{h\nu}{k_B T}\right)^2 \cdot \frac{\exp\left(\frac{h\nu}{k_B T}\right)}{\left[\exp\left(\frac{h\nu}{k_B T}\right) - 1\right]^2} \qquad \ldots (8)$$



Einstein specific heat curve

The Einstein specific heat curve is fairly close to the experimental curve except at low temperature. In this region, the Einstein specific heat approaches zero more rapidly than the observed values. However, at high temperatures, it approaches the classical value. Let us consider the two temperature ranges separately.

High temperature range:

Let us define a quantity $x = h\nu / k_B T$. In this temperature range, $h\nu \ll k_B T$ and therefore, the equation (6) can be written as

$$\bar{\varepsilon} = \frac{h\nu}{e^x - 1}$$

where, $e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \ldots\ldots \cong 1 + x$. Hence, at high temperature,

$$\bar{\varepsilon} = \frac{h\nu}{x} = \frac{h\nu}{h\nu} k_B T = k_B T$$

So that $E = 3N\bar{\varepsilon} = 3Nk_B T$ and $C_V = \left(\frac{dE}{dT}\right)_V = 3Nk_B = 3R$

This is same as the classical result.

Low temperature range:

At low temperatures, $h\nu \gg k_B T$ and hence $e^x \gg 1$. Therefore,

$$\bar{\varepsilon} = \frac{h\nu}{\exp\left(\frac{h\nu}{k_B T}\right)}$$

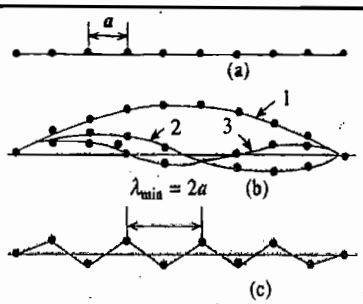
So that $E = 3N\bar{\varepsilon} = 3Nh\nu \exp\left(-\frac{h\nu}{k_B T}\right)$ and $C_V = \left(\frac{dE}{dT}\right)_V = 3Nh\nu\left[-\exp\left(-\frac{h\nu}{k_B T}\right)\cdot\frac{h\nu}{k_B T^2}\right]$

$$= 3Nk_B\left(\frac{h\nu}{k_B T}\right)^2 \exp\left(-\frac{h\nu}{k_B T}\right) \qquad \ldots (9)$$

Equation (9) indicates that the exponential term is more important than the term $\left(h\nu/k_B T\right)^2$ in determining the variation of C_V with temperature. Thus with decreasing temperature, C_V drops exponentially.

The density of states:

One of the important problems of the theory of lattice vibrations is to find out the frequency distribution of normal modes. For the purpose we consider a one-dimensional chain of atoms (string) of length L with fixed ends and that only longitudinal displacement occurs in it. Suppose $u(x, t)$ represents the displacement of string at any point x at a time t. The one dimensional wave equation describing the displacement is



Normal modes of a linear chain of identical atoms (a) linear chain (b) normal modes of the chain (c) normal modes of the chain corresponding to shortest wavelength (to highest frequency)

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 u}{\partial t^2} \qquad \ldots (10)$$

where v is the velocity of the wave in the string. Solving for above boundary conditions (i.e. $u = 0$ at $x = 0$ and $x = L$), the normal mode solutions of equation (10) are obtained in the form of standing waves as

$$u(x,t) = A\sin\left(\frac{n\pi x}{L}\right)\cos 2\pi\nu_n t \qquad \ldots (11)$$

where n is any positive integer ≥ 1 and A is a constant. In such cases, there should be an integral number of half wavelength in the chain, i.e.

$$L = n\frac{\lambda}{2}$$

Differentiating equation (11) with respect to x and t twice, we get

$$\frac{\partial^2 u}{\partial x^2} = -\frac{un^2\pi^2}{L^2} \text{ and } \frac{\partial^2 u}{\partial t^2} = -u4\pi^2\nu^2 \qquad \ldots (12)$$

Substituting these values in equation (10), the frequency can be obtained as

$$\nu^2 = \frac{n^2 v^2}{4L^2} \qquad \ldots (13)$$

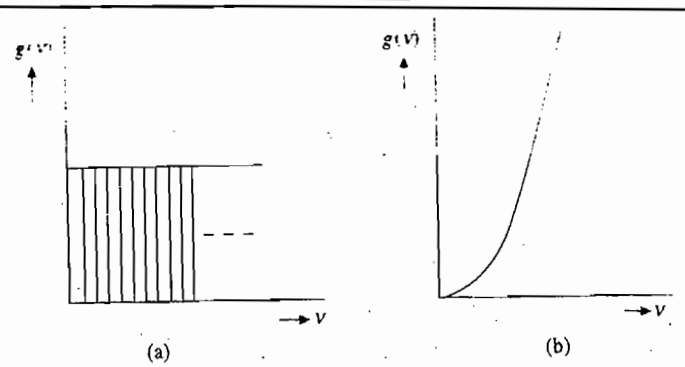
The wavelength and frequencies of the possible vibrations represented by equation (11), are given by

$$\lambda_n = \frac{2L}{n} \text{ and } \nu_n = \frac{v}{\lambda_n} = n\left(\frac{v}{2L}\right) \qquad \ldots (14)$$

The frequency spectrum is discrete, one frequency corresponds to each integer value n. Therefore, the number of possible modes of vibrations $g(\nu)$ in a frequency interval $d\nu$ is, on the average

$$g(\nu) = dn = \frac{2L}{v}d\nu \qquad \ldots (15)$$

According to equation (15), the frequency spectrum corresponds to an infinite number of equidistant lines, as shown in figure (below).



(a) Frequency spectrum for a finite continuous string according to equation (15)
(b) Frequency spectrum for a three-dimensional continuum according to equation (28)

In a three dimensional case, the situation is different. In this case, we have two distinguishable velocities of propagation, v_ℓ for longitudinal wave (a non-degenerate mode) along the direction of propagation and v_t for the transverse wave (doubly degenerate modes) perpendicular to the direction of propagation. Consequently, we have two different equations involving v_ℓ and v_t, each analogous to equation (10), i.e.

$$\frac{\partial^2 u_\ell}{\partial x^2}+\frac{\partial^2 u_\ell}{\partial y^2}+\frac{\partial^2 u_\ell}{\partial z^2}=\frac{1}{v_\ell^2}\frac{\partial^2 u_\ell}{\partial t^2} \qquad \ldots (16)$$

and

$$\frac{\partial^2 u_t}{\partial x^2}+\frac{\partial^2 u_t}{\partial y^2}+\frac{\partial^2 u_t}{\partial z^2}=\frac{1}{v_t^2}\frac{\partial^2 u_t}{\partial t^2} \qquad \ldots (17)$$

Choosing again the simplest boundary conditions that the surface planes of the cube are rigidly held, we obtain the following standing wave solutions

$$u_\ell(x,y,z)=A_\ell \sin\left(\frac{n_x\pi x}{L}\right)\sin\left(\frac{n_y\pi y}{L}\right)\sin\left(\frac{n_z\pi z}{L}\right)\cos 2\pi\nu_l t \qquad \ldots (18)$$

and

$$u_t(x,y,z)=A_t \sin\left(\frac{n_x\pi x}{L}\right)\sin\left(\frac{n_y\pi y}{L}\right)\sin\left(\frac{n_z\pi z}{L}\right)\cos 2\pi\nu_t t \qquad \ldots (19)$$

where n_x, n_y and n_z are positive integers ≥ 1 and A_ℓ and A_t are constants as pointed out earlier.
Differentiating equations (18) and (19) with respect to x, y, z, twice and substituting the resulting values in equations (16) and (17), we obtain the following expressions for the possible modes of vibration,

$$\nu_\ell^2=\frac{v_\ell^2}{4L^2}\left(n_x^2+n_y^2+n_z^2\right) \qquad \ldots (20)$$

and

$$\nu_t^2=\frac{v_t^2}{4L^2}\left(n_x^2+n_y^2+n_z^2\right) \qquad \ldots (21)$$

Thus, for any chosen set of integers, n_x, n_y and n_z, there are three independent modes of the vibrations (one longitudinal and two transverse). Now, employing the relation, $k=\frac{2\pi}{\lambda}=\frac{2\pi\nu}{v}$, the components of the wave vector k from equation (20) can be written as

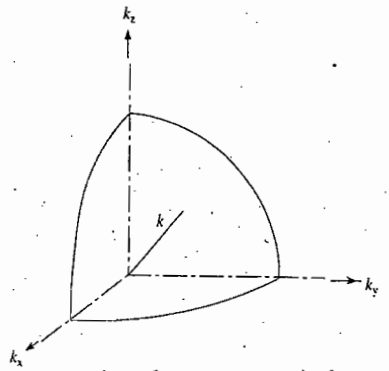
$$k_x=\frac{\pi n_x}{L}, k_y=\frac{\pi n_y}{L}, k_z=\frac{\pi n_z}{L} \qquad \ldots (22)$$

Further, if we suppose that $k^2=k_x^2+k_y^2+k_z^2$, then from equation (20) and (21), it follows that

$$\nu_\ell=\frac{v_\ell k}{2\pi} \text{ and } \nu_t=\frac{v_t k}{2\pi} \qquad \ldots (23)$$

Where k may now be identified as the wave vector with the components k_x, k_y and k_z and r as the position vector. A plot of the allowed values of k in reciprocal space or k-space is shown in figure below. Points defined in equation (22) are distributed as lattice points in the positive octant. The volume of the octant of radius k is

$$\frac{1}{8}\times\frac{4}{3}\pi k^3=\frac{1}{6}\pi k^3$$



Representation of wave vectors in k-space

and the volume occupied by each point is $(\pi/L)^3$. Therefore, the total number of lattice points in the octant is

$$\frac{Vk^3}{6\pi^2}.$$

where $V(=L^3)$ is the volume of the crystal. For a particular frequency ν, the equation (23) will give rise to two wave vectors k_l and k_t as

$$k_l=\frac{2\pi\nu}{v_\ell} \text{ and } k_t=\frac{2\pi\nu}{v_t} \qquad \ldots (24)$$

Thus, the total number of lattice points in the octant with the radii k_l and k_t, respectively are

$$\frac{V}{6\pi^2}\left(\frac{2\pi\nu}{v_\ell}\right)^3 \text{ and } \frac{V}{6\pi^2}\left(\frac{2\pi\nu}{v_t}\right)^3$$

However, since with every lattice point, we may associate one longitudinal mode and two transverse modes, the number of modes $g(\nu)$ of frequency less than ν_D is given by

$$g(\nu)=\frac{8\pi^3V}{6\pi^2}\left(\frac{1}{v_\ell^3}+\frac{2}{v_t^3}\right)\nu^3 \qquad \ldots (25)$$

where a mean velocity v may be defined by the equation

$$\frac{3}{v^3}=\frac{1}{v_\ell^3}+\frac{2}{v_t^3} \qquad \ldots (26)$$

So, that equation (25) becomes, $g(\nu)=\dfrac{4\pi V\nu^3}{v^3}$ ... (27)

Differentiating this expression, we obtain the required frequency distribution fnction

$$g(\nu)d\nu=\frac{12\pi V}{v^3}\nu^2d\nu \qquad \ldots (28)$$

or similarly from equation (25), we obtain,

$$g(\nu)d\nu=4\pi V\left(\frac{1}{v_\ell^3}+\frac{2}{v_t^3}\right)\nu^2d\nu \qquad \ldots (29)$$

This is the number of modes whose frequencies lie between the interval ν and $\nu + d\nu$. A curve between the density of states $g(\nu)$ and ν shows that $g(\nu)$ increases as ν^2. The function $g(\nu)$ is also known as spectral distribution function of normal modes.

Since the number of normal vibrations in a three dimensional crystal lattice is 3*N*, the function $g(\nu)$ should satisfy the following normalization condition.

$$\int_0^{\nu_D} g(\nu)\,d\nu = 3N \qquad \ldots (30)$$

where ν_D is the maximum frequency limiting the spectrum of normal modes from above and is known as Debye frequency. Substituting equation (29) into equation (30) and integrating, we obtain

$$4\pi V\left(\frac{1}{v_\ell^3}+\frac{2}{v_t^3}\right)\int_0^{\nu_D}\nu^2 d\nu = 3N$$

$$\Rightarrow \qquad \nu_D^3 = \frac{9N}{4\pi V}\left(\frac{1}{v_\ell^3}+\frac{2}{v_t^3}\right)^{-1} \qquad \ldots (31)$$

Substituting equation (31) back into equation (29), we obtain the distribution function

$$f(\nu) = \sum_{\ell,t} g(\nu) = \frac{9N}{\nu_D^3}\nu^2$$

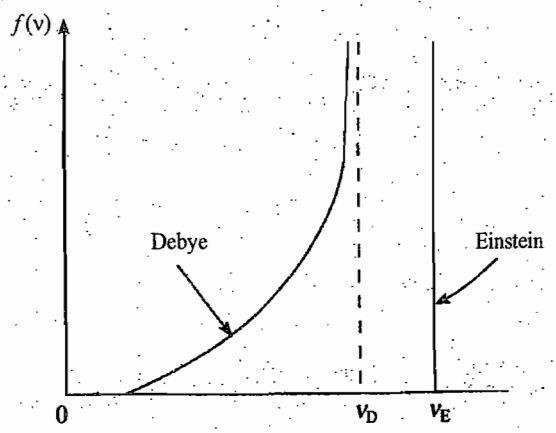
which gives, $\quad f(\nu) = K\nu^2 \quad (\text{for } \nu \le \nu_D) \qquad \ldots (32)$

$$= 0 \quad (\text{for } \nu \le \nu_D)$$

where $K = \dfrac{9N}{\nu_D^3}$ is a constant (independent of ν). This function is compared with the Einstein's function.

The Debye model:

In 1912, Debye pointed out that the source of error lies in the assumption (that all atomic oscillators vibrate independently at a constant frequency) made by Einstein. According to him, the assumption is not justifiable since all atoms are elastically coupled to its neighbours. Debye therefore, simplified the problem by considering a solid as a continuously vibrating medium (as an elastic continuum), which gives rise to a spectrum of frequencies instead of a single frequency as assumed in the Einstein's model. Once, the frequency distribution is known, it is a simple matter to calculate the total internal energy and the hence the specific heat of the solids. Taking into account the density of states as obtained in the preceding section, we can write the internal energy of the Debye solid as



Frequency spectrum according to Debye model and Einstein model

$$E = \int_{\text{all allowed frequencies}} \bar{\varepsilon}(\nu) g(\nu) d\nu \qquad \ldots (33)$$

Using equations (6) and (29), we get

$$E = 4\pi V \left(\frac{1}{v_\ell^3} + \frac{2}{v_t^3}\right) \int_0^{\nu_D} \frac{h\nu \nu^2 d\nu}{\exp\left(\frac{h\nu}{k_B T}\right) - 1}$$

which in terms of equation (31) can be written as

$$E = \frac{9N}{\nu_D^3} \int_0^{\nu_D} \frac{h\nu \nu^2 d\nu}{\exp\left(\frac{h\nu}{k_B T}\right) - 1} \qquad \ldots (34)$$

To simplify equation (34), let us suppose that $x = h\nu / k_B T$, so that $d\nu = (k_B T\, dx)/h$. Further, if we suppose that $x_D = (h\nu_D)/k_B T$, equation (34) becomes

$$E = 9N \left(\frac{k_B T}{h\nu_D}\right)^3 k_B T \int_0^{x_D} \frac{x^3}{e^x - 1} dx \qquad \ldots (35)$$

Now, we can define the Debye temperature as θ_D according to the equation, $h\nu_D = k_B \theta_D$, then

$$\theta_D = \frac{h\nu_D}{k_B} \text{ and } x_D = \frac{\theta_D}{T}$$

So, that equation (35) becomes

$$E = 9Nk_B T \left(\frac{T}{\theta_D}\right)^3 \int_0^{x_D} \frac{x^3}{e^x - 1} dx \qquad \ldots (36)$$

which does not depend explicitly on the volume and looks similar to the expression obtained for Einstein's model. However, let us examine the dependence of the integral (equation 36) on temperature. For simplicity, we shall consider the following two temperature ranges.

High temperature range:

We assumed earlier that $x = h\nu / k_B T$. In this temperature range, $T >> \theta_D$ and hence $k_B T \gg h\nu$ even when $\nu = \nu_D$, implying that x will be small over the whole range of the integration. So, that

$$\int_0^{x_D} \frac{x^3}{e^x - 1} dx \to \int_0^{x_D} \frac{x^3}{x} dx = \frac{x_D^3}{3} = \frac{1}{3}\left(\frac{\theta_D}{T}\right)^3$$

Therefore, $$E = 9Nk_B T \times \frac{1}{3} = 3Nk_B T \qquad \ldots (37)$$

which is the classical result. This implies that in the high temperature range, the specific heat of solids is the same as measured in Dulong and Petit's experiment. This can be understood from the following arguments: when $T >> \theta_D$, every mode of oscillation is completely excited, and has an average energy equal to the classical value i.e. $\bar{\varepsilon} = k_B T$. Substituting this in equation (33) and also making use of the equation (30), we obtain,

$E = 3Nk_BT$, which is same as equation (37).

Low temperature range:

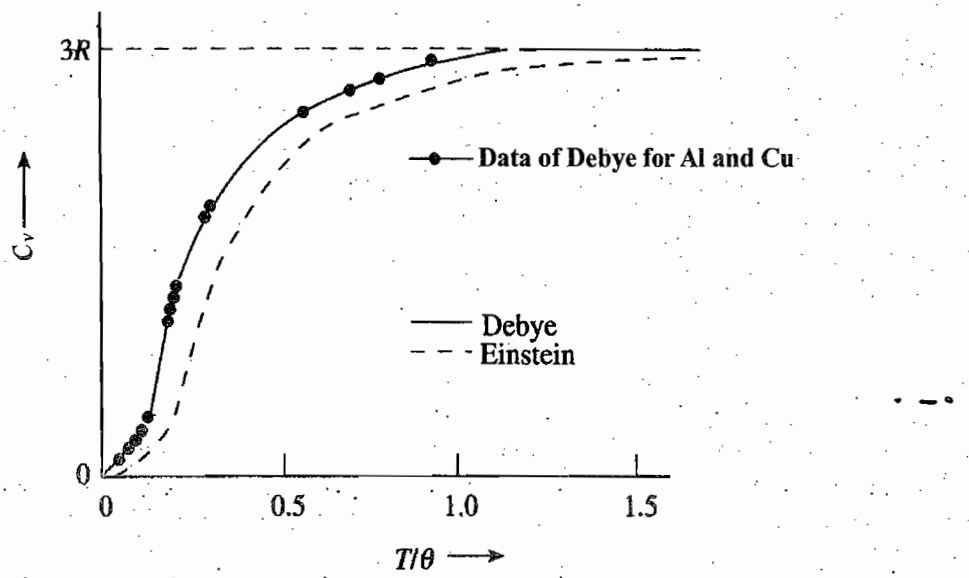
In the low temperature range, $T << \theta_D$, so that $k_BT \ll h\nu_D$. In this case, the upper limit of the integration can be replaced by infinity (i.e. $x_D \to \infty$) and hence the above integral becomes

$$\int_0^{x_D} \frac{x^3}{e^x - 1} dx \to \int_0^{\infty} \frac{x^3}{e^x - 1} dx \to \frac{\pi^4}{15}$$

Therefore, $E = 9Nk_BT\left(\frac{T}{\theta_D}\right)^3 \times \frac{\pi^4}{15} = \frac{3}{5}\pi^4 Nk_BT\left(\frac{T}{\theta_D}\right)^3$

and $$C_V = \frac{12}{5}\pi^4 Nk_B\left(\frac{T}{\theta_D}\right)^3 \quad \ldots (38)$$

This is a famous expression known as Debye T^3 law for specific heat at low temperature. Figure shows a typical Debye plot alongwith the measured data, Einstein plot and the classical value.



Various specific heat curves of a solid

The T^3 dependence can be understood from the following arguments: when $T << \theta_D$, only low frequency normal modes having energy $h\nu < k_BT$ are excited to an appreciable degree. The average energy of these modes may be obtained from equation (6) by expanding the denominator of the expression

$$\bar{\varepsilon}_{n,m} = \frac{h\nu}{\exp\left(\frac{h\nu}{k_BT} - 1\right)} \cong h\nu\left(1 + \frac{h\nu}{k_BT} + \ldots\ldots - 1\right)^{-1} \cong k_BT \quad \ldots (39)$$

This shows that the average energy of every normal mode is proportional to the absolute temperature T (i.e. energy varies linearly with T). In addition to this, the rise in temperature in the low temperature range causes new higher frequency $\left(\nu \cong k_BT / h\right)$ normal modes to be excited. The number of there modes may be calculated using equation (29) and is found to be proportional to $\nu^3 \sim T^3$. Thus in the low temperature range, we observe that the energy of a solid rises with the rise in temperature by means of two mechanisms:

(i) The increase in the average energy of every normal mode, $\bar{\varepsilon}_{n,m}$, proportional to T due to the rise in the probability of its excitation, and

(ii) The increase in number of normal modes of the lattice, proportional to T^3. Therefore, the total energy of excitation is proportional to T^4 and hence a rise in the specific heat is proportional to T^3, which is in agreement with equation (38).

Thermal conductivity of solids:

Thermal conductivity is a process in which heat is transferred from one part of the body to the another as a result of temperature gradient. If the gradient is uniform, then the amount of the thermal energy crossing a unit area in unit time is directly proportional to the temperature gradient, i.e.

$$Q \propto \frac{dT}{dx} \qquad \Rightarrow Q = K\left(\frac{dT}{dx}\right) \qquad \ldots (1)$$

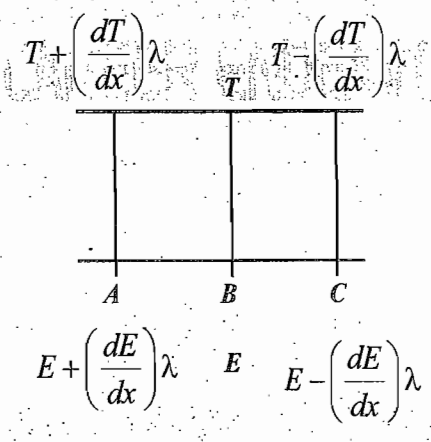
where the proportionality constant K is called the thermal conductivity. In metallic conductors, heat is carried by free electrons, while in insulators, it is mainly carried by phonons. Therefore, in general the transfer of heat can take place both by electrons and phonons and hence the total thermal conductivity can be written as

$$K_{total} = K_{electron} + K_{phonon} \qquad \ldots (2)$$

In order to determine the value of K in equation (1), let us consider a conductor in the form of rod of uniform cross-section (say 1 m^2) with the assumption that there exists a uniform temperature gradient. Let us draw three parallel planes at A, B and C normal to the direction of heat flow which are separated by one mean free path λ as shown in figure below.

According to the kinetic theory, the number of electrons flowing in a given direction through unit area in unit time is $\frac{1}{6}(nv)$, where n is the density of electrons moving with an average velocity v. Further, the excess of energy carried by an electron from plane A to plane B is $\left(\frac{dE}{dx}\right)\lambda$. Thus, the excess energy flowing through the plane B to the right is:

$$Q_{right.} = \frac{1}{6} nv\lambda \left(\frac{dE}{dx}\right) \qquad \ldots (3)$$



Flow of heat through a conductor

Similarly, the energy flowing through the plane B to the left is

$$Q_{left} = -\frac{1}{6} nv\lambda \left(\frac{dE}{dx}\right) \qquad \ldots (4)$$

Therefore, the net amount of energy flowing through the plane B is

$$Q = Q_{right} - Q_{left} = \frac{1}{6} nv\lambda \left(\frac{dE}{dx}\right) - \left[-\frac{1}{6} nv\lambda \left(\frac{dE}{dx}\right)\right] = \frac{nv\lambda}{3}\left(\frac{dE}{dx}\right) \qquad \ldots (5)$$

But $$n\left(\frac{dE}{dx}\right)=n\left(\frac{dE}{dT}\right).\left(\frac{dT}{dx}\right)=nC_v\left(\frac{dT}{dx}\right)$$

where C_v is the specific heat of solid at constant volume. Therefore, equation (5) becomes

$$Q=\frac{nC_v v\lambda}{3}\left(\frac{dT}{dx}\right) \qquad \ldots (6)$$

Now, comparing equations (1) and (6), we obtain

$$K=\frac{1}{3}v\lambda C_v \qquad \ldots (7)$$

Thermal conductivity due to electrons:

In order to derive an expression for thermal conductivity of metals where the heat is predominantly carried by the electrons, we make the following assumptions:

(i) The metal consists of fixed positive ions in a sea of electrons. In general, there will be one or two electrons per ion.

(ii) The electrons behave as a perfect gas and they transport thermal energy from the hotter to the colder region.

(iii) Each electron travels a distance λ in a mean free time τ before colliding with a positive ion where it gives up all its thermal energy.

(iv) Only those electrons that lie within the range k_BT of the Fermi level are active in the transport process. The velocity of such electrons is calculated from the formula.

$$\frac{1}{2}mv_F^2=E_F \qquad \ldots (8)$$

Substituting the value of electronic specific heat $\left(C_e=\frac{\pi^2 Nk_B^2T}{2E_F}\right)$ and $\lambda=v_F\tau$ in equation (7) and making use of equation (8), we obtain the electronic contribution of thermal conductivity as

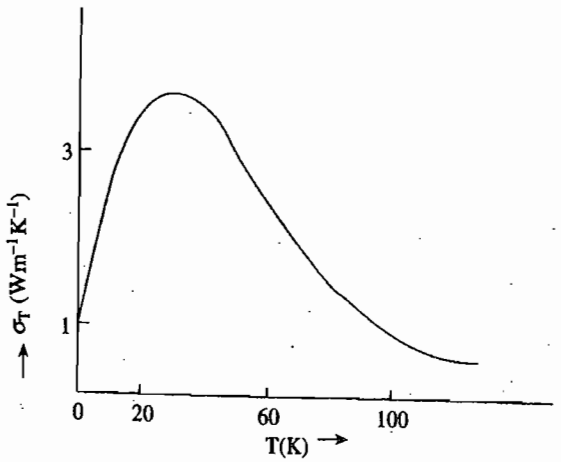
$$K_e=\left(\frac{2\tau E_F}{3m}\right)\left(\frac{\pi^2 Nk_B^{\ 2}}{2E_F}\right)T=\left(\frac{\pi^2 Nk_B^{\ 2}\tau}{3m}\right)T \qquad \ldots (9)$$

Since, the mean free time τ varies as T^{-1} above the Debye temperature, the electronic contribution of thermal conductivity is nearly temperature independent. This is consistent with the experimental facts.

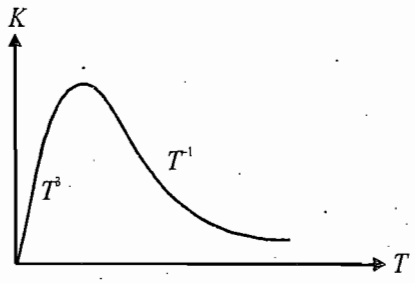
Thermal conductivity due to phonons:

As we know that in insulators, there are no mobile electrons and hence phonons carry most of the heat energy. Thus, for insulators in equation (7), v is the velocity of sound, λ is the phonon mean free path and C_v is the lattice specific heat per unit volume given by the Debye - T^3 law:

$$C_V=\begin{cases}\propto T^3 & (T<\theta_D)\\ 3Nk_B & (T>\theta_D)\end{cases} \qquad \ldots (10)$$



Temperature variation of thermal conductivity for copper



Typical variation of phonon thermal conductivity with temperature

Consequently, the thermal conductivity of an insulator is proportional to T^3 at low temperatures, as shown in figure . At high temperatures $(T >> \theta_D)$, the lattice specific heat is constant (i.e., equal to $3Nk_B$, the Dulong-Petit's value) and any temperature dependence of K arises predominantly from the variation of the mean free path λ due to phonon-phonon interaction (i.e. due to anharmonicity). However, a small contribution may also arise from collisions of phonons with crystal boundaries and impurities. Therefore, for all practical purposes only phonon-phonon contribution is considered. The lattice dynamics of anharmonic crystals which takes into account the phonon-phonon collision is very complicated, but leads to a simple final result, viz. the phonon mean free path is inversely proportional to the absolute temperature, i.e. $\lambda = T^{-1}$, so that,

$$K = T^{-1} \qquad \ldots (11)$$

Thus, the thermal conductivity of an insulator is proportional to T^{-1} at high temperatures.

The Drude theory:

The Drude model assumes that the electrons in a metal are free to move and form an electron gas. The basic assumptions of the Drude model are the following.

(i) The electrons are in thermal equilibrium with the environment.

(ii) Between collisions, the interactions of an electron with the other electrons and with the ions are negligible. Thus the electron travels uniformly in a straight line between collisions in the absence of applied electro-magnetic fields. The motion of electrons in the presence of applied fields is determined by Newton's laws of motion.

(iii) The time taken up in a collision is negligible. The velocity of an electron changes abruptly when it undergoes a collision.

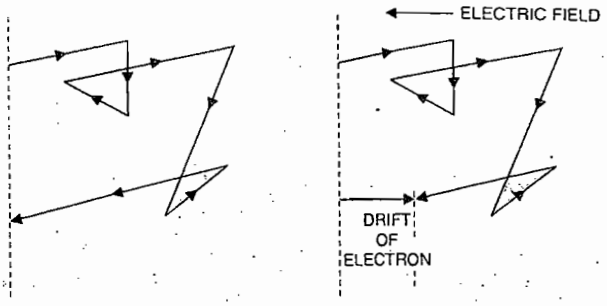
(iv) The electron-electron collisions are usually unimportant.

(v) The metallic ions form the major source of collisions. The exact nature of the scattering is not required; only some broad features associated with the scattering are important. The probability per unit time for an electron to suffer a collision is assumed to be $1/\tau$. The time τ is referred to as the relaxation time, the collision time or the mean free time. For simplicity, τ is taken to be independent of the position and velocity of the electron.

Electrical conductivity:

In the absence of an electric field, the free electrons in a metal move at random owing to their thermal energy. At each collision, the path of the electron is changed. The number of electrons moving in one direction is the same as that moving in the opposite direction, so that considering all the electrons the average drift velocity is zero. When an electric field is applied, the electrons are accelerated between collisions. As an electron carries

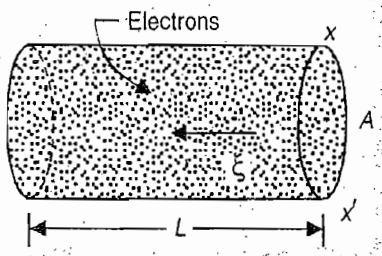
a negative charge the acceleration is opposite to the direction of the field. Immediately after collisions, all the electron velocities are randomised. In equilibrium, all the electrons possess a common drift velocity due to the electric field. The drift velocity has a very small magnitude compared to the random thermal velocity on which it is superimposed. The electron drift gives rise to the current flow through the metal.



(a) Random electron motion, and
(b) electron drift in an applied electric field

The electrical conductivity σ of a solid is the charge conducted per unit time across unit area of the solid for applied unit electric field. If due to an applied electric field ε the current density, i.e. the current per unit cross sectional area is J, the conductivity σ is given by $\sigma = \frac{J}{\varepsilon}$ ... (12)

In S.I. units J is expressed in A/m^2, ε in volt/m, and σ in Siemens/m.



Geometry for calculation of current density

Consider a cylinderical metal of length L and having an area of cross section A (above figure). If v_d is the drift velocity of the electrons for an electric field ε applied along the length of the cylinder, the the time taken by an electron to traverse the distance L as $t = \frac{L}{v_d}$ ... (13)

If n represents the electron concentration then the total number of electrons contained in the cylinder is nAL. The charge inside the cylinder is, therefore, $nALe$, where e is electronic charge. This amount of charge moves through the cross section xx' in time t. Therefore, the current flowing through the metallic cylinder is:

$$I = \frac{nALe}{t} \quad \text{... (14)}$$

The current density J will be $J = \frac{I}{A} = \frac{nLe}{t} = nev_d$ ... (15)

From equations (12) and (15) we get

$$\sigma = ne\frac{v_d}{\varepsilon} \quad \text{... (16)}$$

The quantity v_d / ε, i.e. the drift velocity per unit electric field is termed the mobility of the electron. Denoting the mobility by μ we have, $\sigma = ne\mu$ ... (17)

In SI units, μ is expressed in m^2 / V.s.

Mean free time:

As already mentioned, the probability of an electron suffering a collision in unit time is $1/\tau$. The quantity τ is a constant depending on the system and has the dimension of time.

Consider a group of n_0 electrons at time $t=0$. Let n denote the number of electrons in the group which do not make a collision in time t. If dn be the change in n due to collision in a further time dt, then

$$dn = -\frac{n}{\tau}dt \qquad \ldots (18)$$

$$\Rightarrow \qquad n = n_0 \exp(-1/\tau) \qquad \ldots (19)$$

The mean free time of an electron is given by the total lifetime of all the n_0 electrons divided by n_0. Thus,

$$\text{Mean free time} = -\frac{1}{n_0}\int_0^\infty t\, dn = \frac{1}{\tau}\int_0^\infty t \exp(-1/\tau)dt = \tau \qquad \ldots (20)$$

Thus the quantity τ represents the mean free time of an electron between collisions. The mean free path of an electron is given by $\ell = \tau\bar{v}$ where $\bar{v}$ represents the average velocity of the electron.

During the time between collisions an electron has an acceleration $e\,\varepsilon/m_e$, where e is the electron charge, ε is the electric field, the m_e is the mass of the electron. As an electron, observed at a random instant of time, travels freely on the average for a time τ, the average drift velocity v_d of the electron will be

$$v_d = \frac{e\,\varepsilon\,\tau}{m_e} \qquad \ldots (21)$$

The mobility of the electron is given by $\mu = \frac{v_d}{\varepsilon} = \frac{e\tau}{m_e}$ ... (22)

An order of magnitude of τ can be obtained by noting that for copper $\mu = 3\times10^{-3}$ m^2/V.s. Substituting the values $e = 1.6\times10^{-19}$ coulomb and $m_e = 9.11\times10^{-31}$ kg, we obtain from equation (22), $\tau \approx 1.7\times10^{-14}$ s. The value is however not very accurate since the effective mass of an electron in metal is not exactly equal to the free electron mass. Also, strictly speaking, τ is not a constant but depends on the electron energy. From equations (17) and (22) we express the conductivity σ in the form:

$$\sigma = \frac{ne^2\,\tau}{m_e} \qquad \ldots (23).$$

Thermal conductivity of a metal:

We shall now develop an expression for the thermal conductivity due to free electrons in a metal. Assume a temperature gradient $\frac{dT}{dx}$ in the x-direction. The thermal current density J_q represents the thermal energy crossing a unit area perpendicular to the direction of flow per unit time. It is given by

$$J_q = -K\frac{dT}{dx} \qquad \ldots (24)$$

where K is a positive constant, referred to as the thermal conductivity. The negative sign in equation (24) appears since the heat flow is opposite to the direction of temperature gradient.

After each collision an electron moves with a speed appropriate to the local temperature. Thus an electron emerging from a hotter place of collision will be more energetic. Let $E(T)$ represent the thermal energy of an electron at temperature T. Hence an electron suffering the last collision at the position coordinate x' will

carry on the average a thermal energy $E\left[T(x')\right]$. The electrons that come to the point x from the high temperature side had their last collision at $x' = (x - v_x\tau)$ where v_x is the x-component of the average velocity of the electrons and τ the mean free time. The average thermal energy associated with each such electron is $E\left[T(x - v_x\tau)\right]$. If n be the total number of electrons per unit volume, half of this number will come to the point x from the high-temperatue side and half from the low-temperature side. The thermal current density at x due to the electrons coming from the high-temperature side will be

$$J_{qh} = \frac{n}{2} v_x E\left[T(x - v_x\tau)\right] \quad \ldots (25)$$

Similarly, the thermal current density due to the electrons coming to x from the low temperature side is:

$$J_{q\ell} = \frac{n}{2}(-v_x) E\left[T(x + v_x\tau)\right] \quad \ldots (26)$$

since these electrons move in the negative x-direction. The net thermal current at x is:

$$J_q = J_{qh} + J_{q\ell} = \frac{nv_x}{2}\left[E\left\{T(x - v_x\tau)\right\} - E\left\{T(x + v_x\tau)\right\}\right]$$

It may be assumed that the variation of the temperature over the mean free path $= v_x\tau$ is very small. Thus expanding in a Taylor series and neglecting the higher order terms we get

$$J_q = nv_x^2\tau \frac{dE}{dT}\left(-\frac{dT}{dx}\right) \quad \ldots (27)$$

We shall now replace v_x^2 by its average value $v^2/3$ where v^2 is the mean square velocity. Hence

$$J_q = \frac{1}{3} nv^2\tau \frac{dE}{dT}\left(-\frac{dT}{dx}\right) \quad \ldots (28)$$

If N be the total number of free electrons and V be the volume of the metal we have

$$n\frac{dE}{dT} = \frac{N}{V}\frac{dE}{dT} = C_V \quad \ldots (29)$$

where C_V is the electronic heat capacity per unit volume. Using equation (29) in equation (28) we obtain

$$J_q = -\frac{1}{3} v^2\tau\, C_V \frac{dT}{dx} \quad \ldots (30)$$

Comparing equations (24) and (30) we obtain for the thermal conductivity

$$K = \frac{1}{3} v^2\tau\, C_V = \frac{1}{3}\ell v C_V \quad \ldots (31)$$

From equations (23) and (31) we obtain

$$\frac{K}{\sigma} = \frac{C_V m_e v^2}{3ne^2} \quad \ldots (32)$$

Applying classical gas laws we get, $C_V = \frac{3}{2} m_e v^2 = \frac{3}{2} k_B T$ where k_B is Boltzmann constant. Hence equation (32) reduces to

$$\frac{K}{\sigma} = \frac{3}{2}\left(\frac{k_B}{e}\right)^2 T \quad \ldots (33)$$

Thus the ratio of the thermal and the electrical conductivity is proportional to T and the proportionality constant depends only on the universal constants k_B and e. This result agrees with the Wiedemann-Franz law. The ratio $\frac{K}{\sigma T}$, known as Lorentz number, is found from equation (33) to be

$$\frac{K}{\sigma T} = \frac{3}{2}\left(\frac{k_B}{e}\right)^2 = 1.11\times10^{-8}\ V^2/K^2 \qquad \ldots (34)$$

This value is about one half the typical value for most metals. Although the classical laws cannot be applied to the electron gain a metal, excellent agreement of the Lorentz number with experiments, apart from the factor of 2, is obtained because of cancellation of errors in the electronic contribution to the heat capacity C_V and the mean square electron speed.

SOLVED PROBLEMS

1. While silver metal obeys the Dulong-Petit law at room temperature, the diamond does not, explain.

Soln. According to the Einstein's theory of specific heat, if $h\nu \ll k_B T$, $C_V \to 3R$. For silver, $\nu = 4\times10^{12}$ cycles/sec., so that

$$h\nu = 6.626\times10^{-34}\times4\times10^{12} = 2.65\times10^{-21}\ \text{J}$$

For diamond, $\nu = 2.4\times10^{13}$ cycles/sec, so that

$$h\nu = 6.626\times10^{-34}\times2.4\times10^{13} = 15.9\times10^{-21}\ \text{J}$$

Now, at room temperature, the vlaue of $k_B T$ is found to be

$$k_B T = 1.38\times10^{-23}\times300 = 4.14\times10^{-21}\ \text{J}$$

Comparing these values, we find that for silver the energy $h\nu$ is less than $k_B T$ while for the diamond it is high. The high value of energy (or frequency) is due to strong covalent bonding between the adjacent carbon atoms. As a result, much higher temperature is required for the Dulong-Petit law to obeyed in this case.

2. (i) Calculate Einstein's frequency for copper for which $\theta_E = 230\ K$. Given $h = 6.6\times10^{-34}$ J-sec. Boltzmann constant $k_B = 1.37\times10^{-23}$ Joule/K.
(ii) Use result (i) to show that the classical result $C_V = 3R$ should be valid for copper if $T > 230\ K$.

Soln. **(i)** Einstein's frequency ν_E is given by

$$\frac{h\nu_E}{K} = \theta_E$$

Where h is Planck's constant and k_B is Boltzmann constant

$$h = 6.6\times10^{-34}\ \text{J/sec},\ k_B = 1.37\times10^{-23}\ \text{J/k},\ \theta_E = 230\ K$$

$$\therefore\ \nu_E = \frac{\theta_E k_B}{h} = \frac{230\times1.37\times10^{-23}}{6.6\times10^{-34}} = 4.794\times10^{12}\ \text{sec}^{-1}$$

(ii) $C_V = 3R$ If $T >> \frac{h\nu}{k_B}$

$$\therefore\ \frac{h\nu}{k_B} = \frac{6.6\times10^{-34}\times4.794\times10^{12}}{1.37\times10^{-23}} = 230\ \text{K}$$

2. Calculate Einstein's frequency for a case for which $\theta_E = 236$ K. Given $k_B = 1.4\times10^{-23}$ J/K, $h = 6.6\times10^{-34}$ J/sec.

Soln. $\nu_E = \dfrac{\theta_E k_B}{h} = \dfrac{237\times1.4\times10^{-23}}{6.6\times10^{-34}} = 5\times10^{12}\ \text{sec}^{-1}$.

3. (a) For copper $\nu = 2.49\times10^{12}$ cycles/sec (Hertz). Calculate the characteristic temperature θ_E.
(b) For copper the value of C_V is 23.8 J/mol·K while for Diamond the value of C_V is only 6.1 J/mol·K (both values are at $T = 300$ K). How do you account for this difference?
Given $h = 6.6\times10^{-34}$ J/sec, $k_B = 1.38\times10^{-23}$ J/K.

Soln. (a) The characteristic temperature $\theta_E = \dfrac{h\nu}{k_B} \Rightarrow \theta_E = \dfrac{6.6\times10^{-34}\times2.49\times10^{12}}{1.38\times10^{-23}} = 119.1$ K.

(b) According to Einstein theory, the specific heat of solid $C_V = 3R\left[\dfrac{e^{\theta/T}}{\left(e^{\theta/T}-1\right)^2}(\theta/T)^2\right]$.

where $\theta = \dfrac{h\nu}{k_B}$ is called Einstein's temperature and ν is Einstein's frequency.

Thus, for same temperature T, the values of C_V for copper and diamond differ only due to their different values of frequency ν.

4. For Copper atomic weight 63.5, density 8.95 g/cm^3 and compressibility $\beta = 7.3\times10^{-13}$ cm^2/dyne^{-1}. Using these data and universal constants N, k_B and h deduce the following:
(i) mass m of copper atom.
(ii) the interatomic distance a assuming simple cubic lattice.
(iii) frequency of vibration $\nu = \dfrac{1}{2\pi}\sqrt{\dfrac{3a}{\beta m}}$.
(iv) use result (iii) to show that classical theory result $C_V = 3R$ should be valid for copper if $T >> 230$ K.

Soln. **(i)** Mass of copper atom $m = \dfrac{\text{Atomic weight}}{\text{Avogadro number}} = \dfrac{63.5}{6.02\times10^{23}} = 1.05\times10^{-22}$ g

(ii) Interatomic distance $a = \left(\dfrac{nA}{N\rho}\right)^{1/3}$

here n = lattice points per unit cell = 1 for sc lattice.
A = Atomic weight = 63.5
N = Avogadro number = 6.02×10^{23}
ρ = density of copper = 8.95 gm.cm^{-3}

$\therefore\ a = \left(\dfrac{1\times63.5}{6.02\times10^{23}\times8.95}\right)^{1/3}$

$\log a = \dfrac{1}{3}[\log 63.5 - \log 6.02 - 23 - \log 8.95] = \dfrac{1}{3}[1.8028 - 0.7796 - 23 - 0.9513] = 8.3572$

$a = 2.281\times10^{-8}$ cm $= 2.281$ Å

(iii) $$\nu = \frac{1}{2\pi}\sqrt{\frac{3a}{\beta m}} = \frac{1}{2\times 3.14}\sqrt{\left(\frac{3\times 2.281\times 10^{-8}}{7.3\times 10^{-13}\times 1.05\times 10^{-22}}\right)}$$

$$\log \nu = -\log 2 - \log 3.14 + \frac{1}{2}\left[\log 3 + \log 2.281 - 8 - \log 7.3 - 13 - \log 1.05 + 22\right]$$

$$= 0.3010 - 0.4969 + \frac{1}{2}\left[0.4771 + 0.3581 - 8.9633 + 13 - 0.0212 + 22\right] = 12.6774$$

$$\nu = 4.757\times 10^{12} \text{ cycle/sec}$$

(iv) According to Einstein's theory of specific heat C_V approaches the value $3R$ if $\frac{h\nu}{k_B} << 1$ i.e. if $T > \frac{h\nu}{k_B}$

Here $$\frac{h\nu}{k_B} = \frac{\left(6.62\times 10^{-34}\right)\times\left(4.75\times 10^{12}\ \text{sec}^{-1}\right)}{1.38\times 10^{-23}\ \text{J/K}} = 230\ \text{K}.$$

Therefore, for copper classical theory result $C_V = 3R$ is valid of $T > 230$ K

5. The specific heat C of a certain substance at very low temperature is found to depend on the absolute temperature T according to the relation $C = AT^3$, where A = constant.
(i) If units are calories, gram and Kelvin degree what units must the constant A have?
(ii) How much heat must be added to raise the temperatures of a mass m of the material from T_1 to T_2?

Soln. (i) Given $C = AT^3$ $\quad\therefore\ A = C/T^3$

unit of specific heat is calorie per gm per kelvin and that T is kelvin so unit of A is

$$\frac{\text{calorie per gram per Kelvin}}{(\text{Kelvin})^3} = \text{calorie per gram per } (\text{Kelvin})^4$$

or $\quad \text{cal.gm}^{-1}\ (\text{K})^{-4}$

(ii) Heat required to raise the temperature of mass m of the material by $dT = mC_V dT$. So heat required to raise the temperature of a mass m of the material from T_1 to T_2

$$= \int_{T_1}^{T_2} mC_V dT = \int_{T_1}^{T_2} mAT^3 dT = mA\left[\frac{T^4}{4}\right]_{T_1}^{T_2} = \frac{1}{4}mA\left(T_2^4 - T_1^4\right)$$

6. The Debye temperature of carbon (Diamond) is 1850 K. Calculate the specific heat per K-mol. for diamond at 20 K. Also compute the highest lattice frequency involved in the Debye theory.

Soln. Specific heat at low temperature

$$C_V = 3R\times 12\left(\frac{T}{\theta}\right)^3\frac{\pi^4}{15} = 77.94\times 3R\left(\frac{T}{\theta}\right)^3 = 77.94\times 3R\left(\frac{20}{1850}\right)^3 = 2.45\ \text{J mol}^{-1}\text{K}^{-1}$$

Lattice frequency $$\nu_m = k_B\frac{\theta}{h} = 1.38\times 10^{-23}\times\frac{1850}{6.6\times 10^{-34}} = 3.86\times 10^{13}\ \text{Hz}$$

7. In simple metals the phonon contribution to the electrical resistivity at temperature T is **[GATE 2003]**
(a) directly proportional to T above Debye temperature and below it
(b) inversely proportional to T for all temperatures
(c) independent of T for all temperatures
(d) directly proportional to T above Debye temperature and to T^5 below it

Soln. The phonon contribution to the electrical resistivity at temperature T varies as:

$\rho \propto T$ (at temperatures higher than Debye temperature i.e. $T > \Theta_D$).

and $\rho \propto T^5$ (at temperatures lower than Debye temperature i.e. $T < \Theta_D$).

Hence, correct option is (d).

8. The relaxation time (mean free time), in second of the conduction electrons is **[GATE 2007]**

(a) 3.98×10^{-15} (b) 3.79×10^{-14} (c) 2.84×10^{-12} (d) 2.64×10^{-1}

Soln. Relaxation time $(\tau) = \dfrac{\mu m_e}{e} = \dfrac{6.67 \times 10^{-3} \times 9.1 \times 10^{-31}}{1.6 \times 10^{-19}} = 37.93 \times 10^{-15} = 3.79 \times 10^{-14}$ sec.

Hence, correct option is (b).

9. The lattice specific heat C of a crystalline solid can be obtained using the Dulong-Petit model, Einstein model and Debye model. At low temperature $h\omega \gg k_B T$, which one of the following statements is true (a and A are constants). **[GATE 2008]**

(a) Dulong Petit: $C \propto \exp\left(-\dfrac{a}{T}\right)$; Einstein: C = constant; Debye: $C \propto \left(\dfrac{T}{A}\right)^3$

(b) Dulong Petit: C = constant; Einstein: $C \propto \left(\dfrac{T}{A}\right)^3$; Debye: $C \propto \exp\left(-\dfrac{a}{T}\right)$

(c) Dulong Petit: C = constant; Einstein: $C \propto \dfrac{e^{-a/T}}{T^2}$; Debye: $C \propto \left(\dfrac{T}{A}\right)^3$

(d) Dulong Petit $C \propto \left(\dfrac{T}{A}\right)^3$; Einstein: $C \propto \dfrac{e^{-a/T}}{T^2}$; Debye: C = constant

Soln. According to Dulong-Petit law: $C_V = 3R$ = constant ... (i)

According to Einstein model: $C_V = 3Nk_B \left(\dfrac{\theta_E}{T}\right)^2 e^{-\theta_E/T} \propto \dfrac{e^{-a/T}}{T^2}$ ... (ii)

According to Debye model: $C_V = \dfrac{12}{5}\pi^4 Nk_B \left(\dfrac{T}{\theta_D}\right)^3 \propto \left(\dfrac{T}{A}\right)^3$ ... (iii)

Hence, correct option is (c).

10. The valence electrons do not directly determine the following property of a metal **[GATE 2010]**

(a) electrical conductivity (b) thermal conductivity
(c) shear modulus (d) metallic lustre

Soln. Electrical conductivity, thermal conductivity and metallic lustre properties are valence electron dependent while shear modulus is independent of valence electrons.

Hence, correct option is (c).

11. The thermal conductivity of a given material reduces, when it undergoes a transition form its normal state to the superconducting state. The reason is **[GATE 2010]**

(a) The Cooper pairs cannot transfer energy to the lattice.
(b) upon the formation of Cooper pairs, the lattice becomes less efficient in heat transfer.
(c) The electrons in the normal state loose their ability to transfer heat because of their coupling to the cooper pairs.
(d) The heat capacity increases on transition to the superconducting state leading to a reduction in thermal conductivity.

Soln. The thermal conductivity reduces in the transition from the normal state to the superconducting state because Cooper pairs have very less energy ($\approx 10^{-3}$ eV). They can not transfer energy to the lattice.
Hence, correct option is (a).

12. Which one of the following cannot be explained by considering a harmonic approximation for the lattice vibration in solids? **[GATE 2012]**
(a) Debye's T^3 law (b) Dulong-Petit's law
(c) Optical branches in lattices (d) Thermal expansion

Soln. Expression for potential energy of thermal expansion is given by $U(x) = (cx^2 - gx^3 - fx^4)$. This is a non-harmonic approximation in the lattice vibration in solids.
Hence, correct option is (d).

13. The fermi energies of two metals X and Y are 5 eV and 7 eV and their Debye temperatures are 170 K and 340 K, respectively. The molar specific heats of these metals at constant volume at low temperatures can be written as $(C_V)_X = \gamma_X T + A_X T^3$ and $(C_V)_Y = \gamma_Y T + A_Y T^3$, where γ and A are constants. Assuming that the thermal effective mass of the electrons in two metals are same, which of the following is correct? **[GATE 2016]**

(a) $\frac{\gamma_X}{\gamma_Y} = \frac{7}{5}, \frac{A_X}{A_Y} = 8$ (b) $\frac{\gamma_X}{\gamma_Y} = \frac{7}{5}, \frac{A_X}{A_Y} = \frac{1}{8}$ (c) $\frac{\gamma_X}{\gamma_Y} = \frac{5}{7}, \frac{A_X}{A_Y} = \frac{1}{8}$ (d) $\frac{\gamma_X}{\gamma_Y} = \frac{5}{7}, \frac{A_X}{A_Y} = 8$

Soln. The molar specific heat can be given by

$$C_V = \left(\frac{\pi^2 N_A k_B^2}{2E_F}\right)T + \left(\frac{12\pi^4 N_A k_B}{5T_D^3}\right)T^3 \quad \text{... (i)}$$

$$\Rightarrow \quad C_V = \gamma T + AT^3 \quad \text{... (ii)}$$

$$\text{where, } \gamma = \frac{\pi^2 N_A k_B^2}{2E_F} \Rightarrow \gamma \propto \frac{1}{E_F} \quad \text{... (iii)}$$

$$\text{and } A = \frac{12\pi^4 N_A k_B}{5T_D^3} \Rightarrow A \propto \frac{1}{T_D^3} \quad \text{... (iv)}$$

For X and Y:

$$\frac{\gamma_X}{\gamma_Y} = \frac{\left(\frac{1}{(E_F)_X}\right)}{\left(\frac{1}{(E_F)_Y}\right)} = \frac{(E_F)_Y}{(E_F)_X} = \frac{7\text{ eV}}{5\text{ eV}} = \frac{7}{5} \text{ and } \frac{A_X}{A_Y} = \frac{\left(\frac{1}{(T_D)_X}\right)^3}{\left(\frac{1}{(T_D)_Y}\right)^3} = \frac{(T_D)_Y^3}{(T_D)_X^3} = \left[\frac{(T_D)_Y}{(T_D)_X}\right]^3 = \left(\frac{340}{170}\right)^3 = (2)^3 = 8$$

Hence, correct option is (a).

PRACTICE SET

1. Debye temperatures of copper and gold are 340 K and 170 K, respectively. At room temperature, if the specific heat for copper is 1.5 kJ mol^{-1} K^{-1}, the specific heat for gold is about:
   (a) 0.19 kJ mol^{-1} K^{-1} (b) 1.2 kJ mol^{-1} K^{-1} (c) 1.9 kJ mol^{-1} K^{-1} (d) 12 kJ mol^{-1} K^{-1}

2. The Debye temperature of a metal is 450 K. Its Debye frequency in Hz is of the order of
   (a) 10^{11} (b) 10^{13} (c) 10^{16} (d) 10^{20}

3. At lower temperature, the lattice specific heat varies as
   (a) T^3 (b) $\frac{1}{T^3}$ (c) T (d) $\frac{1}{T}$

4. If there are N atoms in a monatomic solid vibrating with frequency ν, its specific heat at high temperature would be
   (a) $\frac{3Nk_B}{2}$ (b) $3Nk_B$ (c) $5Nk_B$ (d) $\frac{5Nk_B}{2}$

5. Electronic contribution to the specific heat C_V of metals varies as
   (a) $C_V \propto T^3$ (b) $C_V \propto T^2$ (c) $C_V \propto T$ (d) C_V is constant

6. For copper the specific heat of a solid at low temperature has the behaviour of $C_V \cong 4.6 \times 10^{-2} \times T^3$ J mol^{-1} K^{-1}. The Debye temperature for copper is found to be
   (a) 248 K (b) 348 K (c) 448 K (d) 548 K

7. According to Dulong and Petit's law, value of molar lattice specfic heat is
   (a) $\frac{3R}{2}$ (b) $3R$ (c) $\frac{R}{2}$ (d) R

8. According to Debye model heat capacity (C_V) lattice at low temperature varies as proportional to
   (a) T (b) T^3 (c) T^{-1} (d) T^2

9. In one dimensional periodic chain of atoms with lattice parameter 'a' has first brillouin zone at
   (a) a (b) $2a$ (c) $\frac{\pi}{a}$ (d) $\frac{2\pi}{a}$

10. The lattice specific heat C of a crystalline solid can be obtained using the Dulong Petit model, Einstein model and Debye model. At low temperature $h\omega \gg k_B T$, which of the following statements is true (a and A are constants).
    (a) Dulong Petit: $C \propto \exp\left(-\frac{a}{T}\right)$; Einstein: C = constant; Debye: $C \propto \left(\frac{T}{A}\right)^3$
    (b) Dulong Petit: C = constant; Einstein: $C \propto \left(\frac{T}{A}\right)^3$; Debye: $C \propto \exp\left(-\frac{a}{T}\right)$
    (c) Dulong Petit: C = constant; Einstein: $C \propto \frac{e^{-a/T}}{T^2}$; Debye: $C \propto \left(\frac{T}{A}\right)^3$
    (d) Dulong Petit $C \propto \left(\frac{T}{A}\right)^3$; Einstein: $C \propto \frac{e^{-a/T}}{T^2}$; Debye: C = constant

11. If the velocity of sound and the interatomic spacing in a linear monatomic lattice are respectively 3×10^{3} ms^{-1} and 3×10^{-10} m, the cut off frequency in rad/sec, is found to be

(a) 2.14×10^{13} (b) 3.14×10^{13} (c) 4.14×10^{13} (d) 5.14×10^{13}

12. A visible light of wavelength 4000Å undergoes scattering from a diamond crystal of refractive index 2.42. If the velocity of sound in diamond is 1.2×10^{4} ms^{-1}, the maximum frequency of phonon that is generated by it in rad/sec is

(a) 9.12×10^{11} (b) 10.12×10^{11} (c) 11.12×10^{11} (d) 12.12×10^{11}

ANSWER KEY

1. (d)	**2. (b)**	**3. (a)**	**4. (b)**	**5. (c)**	**6. (b)**	**7. (b)**
8. (b)	**9. (c)**	**10. (c)**	**11. (b)**	**12. (a)**		

Chapter 6

FREE ELECTRON THEORY

Classical theory (Free electron gas model): In 1900, Drude and Lorentz have explained the outstanding properties of metals on the basis of free electron model. For free electron model, they have given following assumptions:

(a) A metal consists of positive ion cores and valence electrons. The valence electrons move freely among these ion cores.

(b) Electrons and ions are bound by electrostatic attraction.

(c) The potential of these ion cores is assumed to be constant throughout the metal.

(d) The mutual repulsion between electrons is ignored.

(e) The behaviour of free electrons inside the metals is considered to be similar to that of atoms or molecules in perfect gas. These free electrons are also referred as free electron gas. There are some differences in the molecules of a perfect gas and electrons of free electron gas. The concentration of electrons in the gas is quite large as compared to the concentration of molecules in an ordinary gas. The free electrons are negatively charged while molecules are neutral. The valence electrons also called as conduction electrons and they follow Pauli's exclusion principle. These electrons are responsible for conduction of electricity.

(f) Since, these electrons move in constant electrostatic field of ion cores, there potential energy remains constant and can be taken as zero. Thus, we can ignore the existence of ion cores. Hence, the total energy of free electrons is their kinetic energy. Also, since the movement of conduction electrons is restricted to within the crystal only, the potential energy of a stationary electron inside a metal is less than the potential energy of an identical electron just outside it.

(g) This difference of potential energies serves as a potential barrier and stops the inner electrons from leaving the surface of the metal. Thus, the movement of free electrons in a metal is equivalent to movement of a particle in a potential energy box.

Successes of classical free electron theory:

The free electron model was successful in explaining the following properties:

(1) Ohm's Law: It was successful in explaining Ohm's law. As free electrons move in random directions and do not constitute a current until an electric field is applied across the metal. The electric field accelerates these electrons. During their motion, electrons suffer elastic collisions with the ions which slow down the speed of electrons. This collision gives rise to a steady state current. The magnitude of current is proportional to the voltage applied provided the temperature remains constant. This leads to Ohm's law.

(2) Wiedemann-Franz Law: As the free electrons have ability to move easily inside the metal, the metal exhibit high electrical and thermal conductivity. The ratio of electrical and thermal conductivities is constant for all metals at a constant temperature.

If σ be electrical conductivity and K be the thermal conductivity, then $\boxed{\frac{\sigma}{K} = \text{Constant}}$

This law is known as Wiedemann-Franz law.

(3) Free electron theory also explains the high lustre and complete opacity of metals. The opacity is due to the complete absorption of all the incident electromagnetic radiations by free electrons which are then set into forced oscillations.

Failures of classical free electron theory:

(1) The temperature dependence of resistivity could not be explained. Classical free electron theory predicted resistivity varies as $\sqrt{T}$ whereas actually it is found to vary linearly with temperature.

(2) This theory also failed to explain the heat capacity of solids.

(3) This theory also failed to explain paramagnetic susceptibility of the conduction electrons.

Sommerfeld's quantum theory:

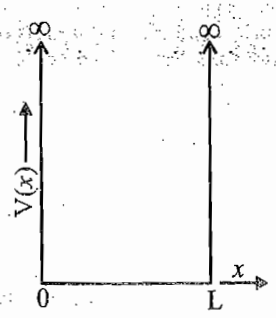
In classical theory, Drude and Lorentz have assumes classical Maxwell-Boltzmann statistics which allows all the free electrons to gain energy. This gives rise to a much higher value of heat capacity and paramagnetic susceptibility.

In 1927, Sommerfeld tried to solve the problem quantum mechanically using the Fermi-Dirac statistics. The possible electronic states in the potential energy box and the distribution of electrons in these states are then determined using quantum mechanics.

Free electron gas in one-dimensional box:

Let us consider an electron of mass m is moving in a potential box of length L. This electron is bound to move within this box under the potential energy given by

$$\begin{cases} V(x) = 0, & \text{for } 0 < x < L \\ V(x) = \infty, & \text{for } x \le 0 \text{ and } x \ge L \end{cases}$$



A one dimensional potential box

Let the wave function ψ_n be the eigen function of n^{th} state. The energy eigen values E_n given by Schrodinger equation

$$\frac{d^2\psi_n}{dx^2} + \frac{2m}{\hbar^2}(E_n - V)\psi_n = 0 \qquad \ldots (1)$$

For the potential box, $V = 0$

Therefore, equation (1) becomes

$$\frac{d^2\psi_n}{dx^2} + \frac{2m}{\hbar^2}E_n\psi_n = 0 \qquad \ldots (2)$$

Let us take, $k^2 = \frac{2mE_n}{\hbar^2}$ thus equation (2) becomes

$$\frac{d^2\psi_n}{dx^2} + k^2\psi_n = 0 \quad \ldots (3)$$

The general solution of the above equation is

$$\psi_n(x) = A\sin kx + B\cos kx \quad \ldots (4)$$

where A and B are constants.

The boundary conditions are

$$\left.\begin{array}{l} \text{at } x = 0, \quad \psi_n(0) = 0 \\ \text{at } x = L, \quad \psi_n(L) = 0 \end{array}\right\} \quad \ldots (5)$$

Using $x = 0, \ \psi_n(0) = 0$ equation (4) $\Rightarrow B = 0$ ... (6)

and using $x = L, \ \psi_n(L) = 0,$ equation (4) $\Rightarrow \psi_n(L) = A\sin kL = 0$

$\Rightarrow \sin kL = \sin n\pi$

$\Rightarrow kL = n\pi \Rightarrow \boxed{k = \frac{n\pi}{L}}$ where, $n = 1, 2, 3.....$ ... (7)

Thus the allowed wavefunction $\psi_n = A\sin\left(\frac{n\pi}{L}\right)x$ ....(8)

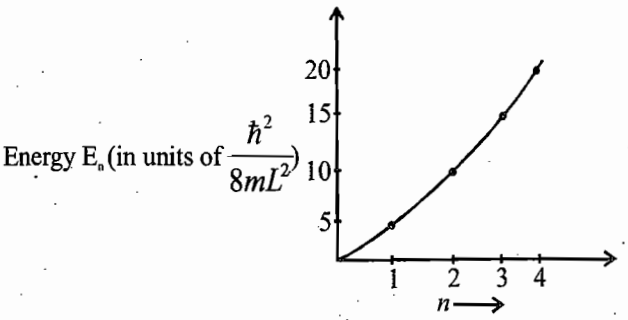
The allowed energy values $E_n = \frac{\hbar^2k^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2$ [using equation (7)]

$\Rightarrow E_n = \frac{n^2\hbar^2\pi^2}{2mL^2} = \frac{n^2h^2}{8mL^2}$

Thus, $\boxed{E_n \propto n^2}$ ... (9)

From equation (9), it is clear that the allowed wavefunction $\psi_n(x)$ and the allowed energy values E_n exist only for integral values of n. This number n is called as quantum number.

Thus the energy spectrum consists of equidistant energy levels and the spacing of energy levels can be determined by n and L. The spacing of energy levels decreases with increasing L. The plot of E_n vs. n is shown in the adjacent figure.



The constant A in equation (8) can be determined using the orthonormality condition such that

$$\int_0^L \psi_n^x(x)\psi_n(x)dx = 1 \qquad \ldots (10)$$

The above condition states that the probability of finding an electron somewhere on the line is unity. Thus,

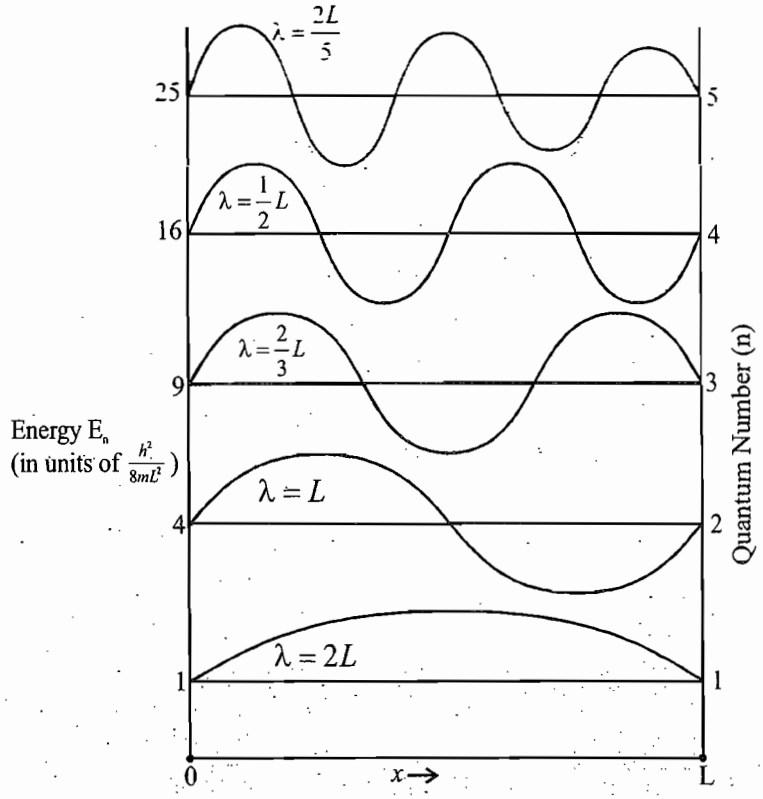
$$\int_0^L \left(A^* \sin\frac{n\pi x}{L}\right)\left(A \sin\frac{n\pi x}{L}\right)dx = 1 \Rightarrow A^* A \int_0^L \sin^2\left(\frac{n\pi x}{L}\right)dx = 1$$

$$\Rightarrow |A|^2 \int_0^L \left\{1 - \cos\left(\frac{2n\pi}{L}x\right)\right\}dx = 1 \Rightarrow \frac{|A|^2}{2}\int_0^L dx = 1 \Rightarrow \frac{|A|^2}{2}[x]_0^L = 1 \Rightarrow \frac{|A|^2}{2}\cdot L = 1$$

$$\Rightarrow A = \sqrt{\frac{2}{L}} \qquad \ldots (11)$$

Thus equation (8) $\Rightarrow \psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)$ ... (12)

The wave functions corresponding to $n = 1, 2, 3, 4$ and 5 are shown in above figure.



In further sections, we will determine the Fermi energy and density of states.

Fermi energy:

The distribution of electrons among the various possible energy levels is governed by Pauli's exclusion principle which states that "no two electrons can have all their quantum numbers identical". Thus, each orbital or state can be occupied by at the most one electron. In a solid, an electron in a conduction electronic state has the quantum numbers n and m_s where n is the principal quantum number and m_s is the magnetic spin quantum number. Each set of values of n and m_s define a quantum state. For each value of n, m_s can take values, $+\frac{1}{2}$ and $-\frac{1}{2}$. This means that each energy level defined by the quantum number n can have two quantum states and hence can accommodate maximum two electrons.

These electrons will have spin $+\frac{1}{2}$ (up) and $-\frac{1}{2}$ (down). In other words, each energy level is doubly degenerate. For example, if there are 9 electrons of appropriate spins, then in ground state, these electrons can be accommodated in 5 energy levels, the first four levels will have two opposite spin electrons and last level will have last unpaired ninth electron. Thus, we find that energy levels with $n < 5$ will be occupied and the levels with $n > 5$ will be empty.

The topmost filled energy level at 0 K is called as the Fermi level and the energy of this level is known as the Fermi energy (E_f).

Let, N be the total number of electrons to be accommodated the line, then for even N, we can write.

$$2n_f = N$$

where, n_f represents the principal quantum number of the fermi level. Thus, for $n = n_f$, equation (9) gives.

$$E_f = \frac{\hbar^2}{2m}\left(\frac{n_f \pi}{L}\right)^2 \quad \Rightarrow \boxed{E_f = \frac{\hbar^2}{2m}\left(\frac{N\pi}{2L}\right)^2} \qquad \ldots (13)$$

Thus, the value of the Fermi energy depends upon the length of the box and the number of electrons in the box.

For example, if we take $\frac{N}{L} = 0.5$ electrons / A°

$= 5 \times 10^7$ electrons / cm

Thus, if we accommodate 5×10^7 electrons on one cm. length of the line, the energy of the top most electron would be 2.4 eV.

Total energy:

The total energy (E_0) of all the N electrons in the ground state is given by

$$E_0 = 2\sum_{n=1}^{N/2} E_n \qquad \ldots (14)$$

Here, the factor of 2 represents that each level contains two electrons with equal energy.

From using equations (13), equation (14) becomes,

$$E_0 = 2\frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 \sum_{n=1}^{N/2} n^2 \qquad \ldots (15)$$

Since, $\sum_{n=1}^{s} n^2 = \frac{s(s+1)(2s+1)}{6} = \left(\frac{2s^3+3s^2+s}{6}\right) \cong \frac{1}{3}s^3$ for $s \geq 1$

$$\therefore \quad \sum_{n=1}^{N/2} n^2 \cong \frac{1}{3}\left(\frac{N}{2}\right)^3$$

Hence, equation (15) becomes $E_0 = 2\frac{\hbar^2}{2m}\cdot\left(\frac{\pi}{L}\right)^2 \cdot \frac{1}{3}\left(\frac{N}{2}\right)^3 = \frac{1}{3}\frac{\hbar^2}{2m}\cdot\left(\frac{N\pi}{2L}\right)^2 N$

Using equation (13), we obtain

$$\boxed{E_0 = \frac{1}{3}NE_f} \qquad \ldots (16)$$

Hence, for one-dimensional crystal, the average kinetic energy is given by $\bar{E} = \frac{E_0}{N}$

$$\Rightarrow \quad \boxed{\bar{E} = \frac{1}{3}E_f} \qquad \ldots (17)$$

i.e. average kinetic energy is one-third of the fermi energy.

Density of states D(E):

The density of states is defined as the number of electronic states present in a unit energy range. It is denoted by $D(E)$.

Thus, $D(E) = \frac{dn}{dE}$ ... (18)

where dn is the number of electronic quantum states present in energy interval E and $E + dE$.

Since, for a free electron gas, each energy level has two electronic states, therefore the actual density of states is twice the value given in equation (18).

Thus, we have $D(E) = 2\frac{dn}{dE}$ ... (19)

Since equation (9) $\Rightarrow E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2$

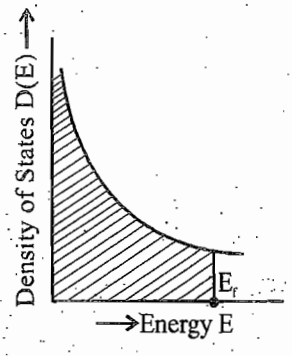
$$\Rightarrow \frac{dE}{dn} = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)2n = \frac{\hbar^2 n}{4mL^2}$$

Therefore, equation (19) gives

$$D(E) = 2\left(\frac{4mL^2}{n\hbar^2}\right) = \left(\frac{8mL^2}{\hbar^2}\right)\left(\frac{1}{n}\right)$$

Again from equation (9), we get $\frac{1}{n} = \left(\frac{\hbar^2}{8mL^2E}\right)^{1/2}$

Hence, density of states $D(E) = \left(\frac{8mL^2}{\hbar^2 E}\right)^{1/2} = \frac{4L}{\hbar}\left(\frac{m}{2E}\right)^{1/2}$ ... (20)



The plot of $D(E)$ versus E is shown in adjacent figure. This graph shows that the level below the Fermi-level are filled and all those are above it are empty. This type of situation exists at only absolute 0 K. Thus, we can say at 0 K, the Fermi-level divides the filled and unfilled levels in the metals.

Free electron gas in three dimensions:

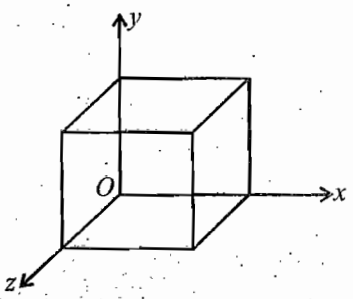
Let us now consider the behaviour of the free electron gas in three-dimensional metallic crystal. The potential of the electrons inside the crystal can be taken as zero, whereas it has a large value outside the crystal.

For the sake convenience, the three-dimensional crystal may be regarded as a cubical box having length of the edge equal to L.

The Schrodinger equation in three dimensions can be written as

$$\frac{-\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]\psi_k(\vec{r})=E_k\psi_k(\vec{r}) \qquad \ldots (21)$$

$$\Rightarrow \nabla^2\psi_k(\vec{r})+\frac{2m}{\hbar^2}E_k\psi_k(\vec{r})=0$$



Three dimensional potential box

where, $\nabla^2 \equiv \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$ is the Laplacian operator and E_k is the total energy of the electron in the k-state. The total energy is the kinetic energy in this case.

The wave function (normalized) for the cubical box of side L can be written as

$$\psi_k(\vec{r})=\sqrt{\frac{2}{L}}\sin\left(\frac{n_x\pi x}{L}\right)\sqrt{\frac{2}{L}}\sin\left(\frac{n_y\pi y}{L}\right)\sqrt{\frac{2}{L}}\sin\left(\frac{n_z\pi z}{L}\right) \qquad \ldots (22)$$

$$=\sqrt{\frac{8}{L^3}}\sin\left(\frac{n_x\pi x}{L}\right)\sin\left(\frac{n_y\pi y}{L}\right)\sin\left(\frac{n_z\pi z}{L}\right) \qquad \ldots (22)$$

where, n_x, n_y and n_z are positive integers and $\sqrt{\frac{8}{L^3}}$ is the normalizing constant for this case.

The allowed eigen values of the state or orbital with wave vector $\vec{k}$ are given by

$$E_k=\frac{\hbar^2k^2}{2m}=\frac{\hbar^2}{2m}(k_x^2+k_y^2+k_z^2) \qquad \ldots (23)$$

where the magnitude of the wave vector $\vec{k}$ is related to the wavelength λ as $k=\frac{2\pi}{\lambda}$.

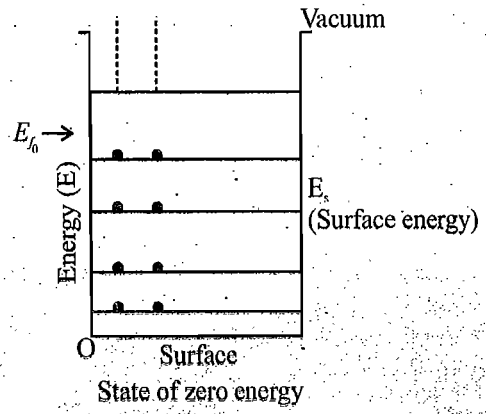
Filling of energy levels:

Since, the distribution of electrons in the allowed energy levels follows the Pauli's exclusion principle. Here in this case we have four quantum numbers k_x, k_y, k_z and m_s which represents a state of the system. From the equation (23), it is clear that a set of values of k_x, k_y and k_z defines an energy level. For each set of k_x, k_y and k_z, the fourth quantum number m_s can have two values $+\frac{1}{2}$ and $-\frac{1}{2}$

Hence each energy level contains two quantum states and thus can accommodate a maximum of two electrons, one with spin up and other with spin down or we can say each energy level is doubly degenerate. Hence a total of N non-interacting electrons at 0 K can be filled in $N/2$ energy levels.

The $\left(\frac{N}{2}\right)^{th}$ level is the top most level and all the levels below this are filled and above it are empty. This level is known as fermi level and energy of this level is denoted by E_{f_0}.

The distribution of electrons is shown in figure. Thus, it is clear that the Sommerfeld's quantum theory does not allow the condensation of all the electrons into the state of zero energy even at absolute zero.



Effect of temperature on the occupancy of energy levels:

At 0 K, the topmost filled level is the fermi level. At temperatures greater than 0 K, the Fermi-level may not be the topmost filled level because some of the electrons from the filled energy levels may be excited to higher levels. So there will be some empty levels below E_{f_0} and some occupied level above E_{f_0}.

The probability that a particular state with energy E is occupied at temperature T is given by following function.

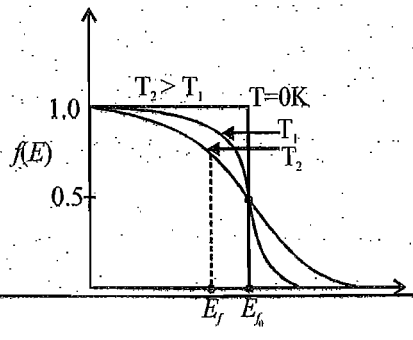
$$f(E) = \frac{1}{\exp\left(\frac{E - E_f}{k_B T}\right) + 1} \qquad \ldots (24)$$

where, E_f is the fermi energy. The function $f(E)$ is called as Fermi-Dirac distribution function.

The plot of $f(E)$ versus E is represented in the adjacent figure.

At $T = 0K$, the equation (24) gives

$$\begin{cases} f(E) = 1 & \text{for } E \le E_{f_0} \\ = 0 & \text{for } E > E_{f_0} \end{cases}$$



which confirms that all the energy states below E_{f_0} have hundred percent probability i.e. are occupied states and states above E_{f_0} are empty. Hence, the Fermi-Dirac distribution function is exactly a step function.

For $T > 0K$ and $T <$ melting point of the metal such that $k_B T \ll E_f$, the Fermi-Dirac distribution function loses its step character. The probability $f(E)$ will decreases from 1 to zero near E_f. This confirms that some of the states below E_f are empty and some states above are filled. This is because some electrons from the energy states below E_f gain thermal energy and get excited to the states above E_f.

At $E = E_f$, equation (24) gives $f(E_f) = \frac{1}{2}$

Thus, we can define the fermi levels as a level where the value of $f(E)$ i.e. probability of occupation is $\frac{1}{2}$. Now, the position of the fermi level is not E_{f_0}. It changes with temperature. An approximate relationship between E_f and E_{f_0} is given by:

$$E_f \equiv E_{f_0}\left[1 - \frac{\pi^2}{12}\left(\frac{k_B T}{E_{f_0}}\right)^2\right] \qquad \ldots (25)$$

For metals, the spacing between the levels is quite small ($\sim 10^{-19}$ eV), the highest filled energy level is usually taken as the fermi level (E_f).

Density of states [$D(E)$] : :

The density of states $[D(E)]$ is defined as the total number of available electronic states (or orbitals) per unit energy range at energy E. To obtain the expression for $D(E)$, we consider the linear momentum $\vec{p}$ as follows.

$$\vec{p} = -i\hbar\nabla$$

For wave function $\psi_k(\vec{r})$, $\vec{p}\psi_k(r) = -i\hbar\nabla\psi_k(\vec{r}) = \hbar k\psi_k(\vec{r})$

which confirms that the plane wave function ψ_k is an eigen function of the linear momentum with the eigen value $\hbar\vec{k}$. The particle velocity is $\vec{v} = \frac{\hbar\vec{k}}{m}$.

For a system of N free electrons, the occupied states orbitals in the ground state can be shown by points inside a sphere in the $\vec{k}$ -space. The energy corresponding to the surface of the sphere represents the Fermi energy. Let $\vec{k}_f$ be the wave vector from the origin of the k-space to the surface of the sphere as shown in figure. Thus from equation (23), the Fermi energy is written as

$$E_f = \frac{\hbar^2 k_f^{\,2}}{2m} \qquad \ldots (26)$$

Density of states for free electron gas:

For electrons in a metal or gas molecules in a container, the value of l is so large that the energy levels can be regarded as forming a continuous spectrum. For this case determine the number of states (n_x, n_y, n_z) with energies in the interval between E and $E + dE$.

The problem here is very similar to that of the blackbody problem. Writing $N = \sqrt{n_x^2 + n_y^2 + n_z^2}$; we obtain for the number of states, dS, with energies between E and $E + dE$

$$dS = \frac{1}{8}\left(4\pi N^2 dN\right) = \frac{\pi}{2} N^2 dN$$

From energy of cubic box, $N^2 = n_x^2 + n_y^2 + n_z^2 = E\left(\frac{8m\ell^2}{h^2}\right)$

So, that $\quad N = \left(\frac{8m\ell^2}{h^2}\right)^{1/2} E^{1/2} \qquad dN = \left(\frac{8m\ell^2}{h^2}\right)^{1/2} \frac{dE}{dE^{1/2}}$

And, $\quad dS = \frac{\pi}{2} E\left(\frac{8m\ell^2}{h^2}\right)\left(\frac{8m\ell^2}{h^2}\right)^{1/2}\left(\frac{dE}{2E^{1/2}}\right) = \frac{2\pi\ell^3 (2m)^{3/2}}{h^3} E^{1/2} dE$

Thus, the density of states in the energy interval dE is, with $V = \ell^3$

$$g(E) = \frac{2\pi V (2m)^{3/2}}{h^3} E^{1/2}$$

Fermi energy at $T = 0$

The density of states between energy E and $E + dE$ is:

$$dS = g(E)\,dE = \frac{2\pi V (2m)^{3/2}}{h^3} E^{1/2} dE$$

Since for each set of quantum numbers (n_x, n_y, n_z) there are two possible electron spin orientations, we must multiply $g(E)$ by a factor of 2 to get the actual density of states for the electron gas. Thus, the total number N of fermions in the system is given by

$$N = 2\int_0^\infty f(E) g(E)\,dE = \frac{4\pi V (2m)^{3/2}}{h^3} \int_0^\infty \frac{E^{1/2} dE}{e^{(E - E_f)/k_B T} + 1}$$

At $T = 0$ K the Fermi-Dirac distribution function is

$$f(E) = 1 \quad \text{for } E < E_f \quad \text{and} \quad f(E) = 0 \quad \text{for } E > E_f$$

So, the limits on the integral can be changed, to give

$$N = \frac{4\pi V (2m)^{3/2}}{h^3} \int_0^{E_f} E^{1/2} dE = \frac{4\pi V (2m)^{3/2}}{h^3}\left(\frac{2}{3} E_f^{3/2}\right)$$

Or, $$E_f = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3}$$

Density of states in Photon gas:

Consider, for simplicity, a cubic cavity of side l whose edges define a set of axes and whose walls are maintained at a temperature T. Maxwell's equations for electromagnetic waves show that the rectangular components of the wave vector.

$$k = \frac{2\pi}{\lambda^2}\lambda$$

must satisfy the boundary conditions,

$$\frac{k_x \ell}{\pi} = n_x, \quad \frac{k_y \ell}{\pi} = n_y, \quad \frac{k_z \ell}{\pi} = n_z$$

where n_x, n_y, and n_z are positive integers. (These boundary conditions ensure an integral number of half waves in each edge of the cube.) Each triplet (n_x, n_y, n_z) represents, in classical terms, an electromagnetic mode of oscillation for the cavity; we shall consider these modes as photon states. Find the number of modes in the frequency interval between ν and $\nu + d\nu$, given that there are two independent polarization directions for each mode.

Each allowed freuqency v corresponds to a certain mode (n_x, n_y, n_z) and can be written as

$$\nu = \frac{c}{\lambda} = \frac{ck}{2\pi} = \frac{c}{2\ell}\sqrt{n_x^2 + n_y^2 + n_z^2} = \frac{cN}{2\ell}$$

where $N = \sqrt{n_x^2 + n_y^2 + n_z^2}$. Instead of trying to find the number of integer states (n_x, n_y, n_z) corresponding to a given N, we use a continuous approximation and find the number of points in a spherical shell of radius N and thickness dN in the first octant of (n_x, n_y, n_z) space. This is the "volume".

$$dM = \frac{1}{8}\left(4\pi N^2 dN\right) = \frac{\pi}{2}N^2 dN$$

But the number of states between N and $N + dN$ must equal the number of states in the corresponding frequency interval, ν to $\nu + d\nu$. Using $\nu = cN / 2\ell$

$$dN = \frac{2\ell}{c}d\nu$$

From which $$dM = \frac{\pi}{2}\left(\frac{2\ell\nu}{c}\right)^2\left(\frac{2\ell}{c}d\nu\right) = \frac{4\pi\ell^3}{c^3}\nu^2 d\nu = g(\nu)d\nu$$

Thus, the density of photon states in a frequency interval $d\nu$ is

$$g(\nu) = \frac{8\pi V}{c^3}\nu^2$$

Average kinetic energy $(\bar{E}_0)$

Average K.E. of an electron E_0 if given by an expression

$$\bar{E}_0 = \frac{1}{N}\int_0^\infty E.g(E)\cdot f(E)\,dE$$

Where $g(E) = c\sqrt{E}$ and using the result, $f(E) = 1$ for $E < E_f$ and $f(E) = 0$ for $E > E_f$ at $T = 0$ K, we get

$$\bar{E}_0 = \frac{1}{N}\int_0^{E_f} E.C\sqrt{E}\,dE + \frac{1}{N}\int_{E_f}^{\infty} E.C\sqrt{E}.0.dE = \frac{2}{5}\frac{C}{N}E_f^{5/2} \quad \ldots (1)$$

Now $CE_f^{1/2} = g(E_f)$ and $g(E_f) = \frac{3}{2}\frac{N}{E_f}$

Combining the two, we get $CE_f^{1/2} = \frac{3}{2}\frac{N}{E_f}$ or $\frac{C}{N} = \frac{3}{2}\frac{1}{E_f^{3/2}}$

$$\bar{E}_0 = \frac{2}{3}.\frac{3}{2}.\frac{1}{E_f^{3/2}}E_f^{5/2} \quad \ldots (2)$$

Substituting equation (2) in equation (1) we get, $\bar{E}_0 = \frac{3}{5}E_f$

$\therefore$ Kinetic energy of N free electron $= \frac{3}{5}NE_f$

Thus, the kinetic energy of a three dimensional gas of N free electrons at 0 K is

$$E_0 = \frac{3}{5}NE_f$$

Property	1-D	2-D	3-D
(i) Fermi energy[E_f]	$\frac{\hbar^2}{2m}\left(\frac{N\pi}{2L}\right)^2$	$\frac{\hbar^2\pi N}{mA}$	$\frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$
(ii) Density of state[$D(E)$]	$\frac{4L}{\hbar}\left(\frac{m}{2E}\right)^{1/2}$	$\frac{mA}{\hbar^2\pi}$	$\frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}E^{1/2}$
(iii) Average K.E.[E]	$\frac{1}{3}E_f$	$\frac{1}{2}E_f$	$\frac{3}{5}E_f$
(iv) Fermi wave vector[k_f]	$\left(\frac{N\pi}{2L}\right)$	$\left(\frac{2\pi N}{A}\right)^{1/2}$	$\left(\frac{3\pi^2 N}{V}\right)^{1/3}$
(v) Fermi velocity[v_f]	$\frac{\hbar}{m}\left(\frac{N\pi}{2L}\right)$	$\frac{\hbar}{m}\left(\frac{2\pi N}{A}\right)^{1/2}$	$\frac{\hbar}{m}\left(\frac{3\pi^2 N}{V}\right)^{1/3}$

Where, $E_f = \frac{P_f^2}{2m}$, $P_f = \hbar k_f$, $v_f = \frac{P_f}{m}$, $T_f = \frac{E_f}{k_B}$

SOLVED PROBLEMS

1. The probability that a state which is 0.2 eV above the Fermi energy in a metal atom at 700 K is
(a) 96.2% (b) 62.3% (c) 3.5% (d) 37.7%

Soln. Probability of occupancy of a given state with energy E is given by the Fermi-Dirac distribution function, which is

$$f(E)=\frac{1}{\left[1+\exp\left(\frac{E-E_f}{k_BT}\right)\right]}=\frac{1}{\left[1+\exp\left(\frac{0.2\times1.6\times10^{-19}}{1.38\times10^{-23}\times700}\right)\right]}$$

$$=\frac{1}{1+\exp\left(\frac{0.32\times10^{-19}}{1.38\times7\times10^{-21}}\right)}=\frac{1}{\left[1+\exp\left(\frac{32}{9.66}\right)\right]}$$

$$=\frac{1}{\left[1+\exp(3.313)\right]}=\frac{1}{(1+27.46)}=0.035$$

$\therefore$ % Probability = 3.5%

Hence, correct option is (c).

2. The potential in a divalent solid at a particular temperature is represented by a one-dimensional periodic model. The solid should behave electrically as **[GATE 2002]**

(a) a semiconductor (b) a conductor (c) an insulator (d) a superconductor

Soln. Divalent solids are Alkaline earth metals. They behave like a conductor.

Hence, correct option is (b).

3. For an ideal Fermi gas in three-dimensions, the electron velocity v_F at the Fermi surface is related to electron concentration n as **[GATE 2012]**

(a) $v_F \propto n^{1/2}$ (b) $v_F \propto n$ (c) $v_F \propto n^{2/3}$ (d) $v_F \propto n^{1/3}$

Soln. The Fermi energy of a Fermi gas can be given as

$$E_F=\frac{\hbar^2}{2\pi}\left(2\pi^2 n\right)^{2/3} \Rightarrow E_F \propto n^{2/3} \quad \text{...(i)}$$

Now, this Fermi energy is related to velocity v_F at the Fermi surface as $E_F=\frac{1}{2}mv_F^2$

$$\Rightarrow \frac{1}{2}mv_F^2=\frac{\hbar^2}{2m}\left(2\pi^2 n\right)^{2/3} \Rightarrow v_F^2 \propto n^{2/3} \Rightarrow v_F \propto n^{1/3}.$$

Hence, correct option is (d).

4. A proton is confined to a cubic box, whose sides have length 10^{-12} m. What is the minimum kinetic energy of the proton ? The mass of proton is 1.67×10^{-27} kg and Planck's constant is 6.63×10^{-34} J-sec.

(a) 1.1×10^{-17} J (b) 3.3×10^{-17} J (c) 9.9×10^{-17} J (d) 6.6×10^{-17} J **[GATE 2013]**

Soln. Sides of box = 10^{-12} m

Charge of proton = 1.6×10^{-19} coulomb

Mass of proton $(m_p)=1.67\times10^{-27}$ kg

Planck's constant $h = 6.63 \times 10^{-34}$ J-s

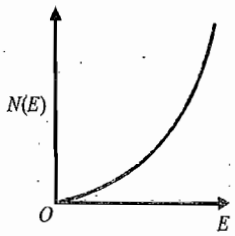
$$\text{Minimum K.E.}\,(E_K) = \left(\frac{\hbar^2}{2m}\right)\frac{\pi^2}{L^2}\left(n_x^2 + n_y^2 + n_z^2\right) = \frac{h^2 \cdot 3}{8mL^2} \quad (n_x = n_y = n_z = 1 \text{ for minimum energy})$$

$$= \frac{(6.63 \times 10^{-34})^2 \times 3}{8 \times 1.67 \times 10^{-27} \times (10^{-12})^2} = 3 \times 3.29 \times 10^{-17} = 9.9 \times 10^{-17}\ \text{J}.$$

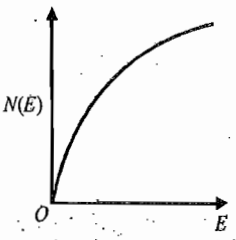
Hence, correct option is (c).

5. For a free electron gas in two dimensions, the variation of the density of states, $N(E)$ as a function of energy E is best represented by **[GATE 2014]**

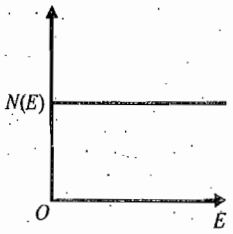
(a)



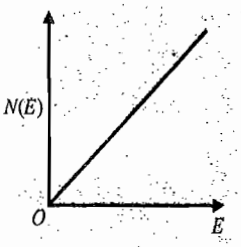
(b)



(c)

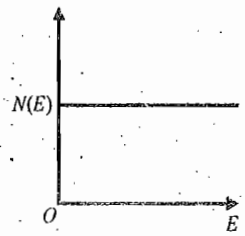


(d)



Soln. Since the density of states, $N(E)$ is independent of energy (E) for a free electron gas in two dimensions.

$\therefore$ $N(E)$ versus E graph can be represented as



Hence, correct option is (c).

6. The energy dependence of the intensity of states for a two dimensional non-relativistic electron gas is given by $g(E) = CE^n$, where C is constant. The value of n is _____. **[GATE 2015]**

Soln. The energy dependence of the density of states for two dimensional non-relativistic electron gas is given by

$$g(E) = CE^n \qquad \ldots (i)$$

The density of states for two dimensional electron gas is independent of energy.

$$g(E) \propto E^0 \qquad \ldots (ii)$$

Comparing equation (i) and equation (ii), we get $\boxed{n = \text{zero}}$.

Hence, correct answer is (0).

7. Given that the Fermi energy of gold is 5.54 eV, the number density of electrons is _____ $\times 10^{28}$ per m^3 (upto one dimensional place). **[GATE 2015]**

[Mass of electron = 9.11×10^{-31} kg, $h = 6.626 \times 10^{-34}$ J-s, 1 eV = 1.6×10^{-19} J]

Soln. The Fermi energy (E_F) is given by $E_F = \frac{h^2}{2m}\left(\frac{3N}{8\pi V}\right)^{2/3}$

$$\Rightarrow E_F = \frac{h^2}{2m}\left(\frac{3}{8\pi}n\right)^{2/3} \qquad \left[\text{Let } \frac{N}{V} = n = \text{electron density}\right]$$

$$\Rightarrow \left[\frac{3n}{8\pi}\right]^{2/3} = \frac{2mE_F}{h^2}$$

$$\Rightarrow \left(\frac{3n}{8\pi}\right) = \left(\frac{2mE_F}{h^2}\right)^{3/2}$$

$$\Rightarrow n = \frac{8\pi}{3} \times \left(\frac{2mE_F}{h^2}\right)^{3/2} = \left(\frac{8 \times 3.14}{3}\right) \times \left(\frac{2 \times 9.11 \times 10^{-31} \times 5.54 \times 1.6 \times 10^{-19}}{(6.626 \times 10^{-34})^2}\right)^{3/2}$$

$$= 8.373 \times \left[\frac{3.6785 \times 10^{-50}}{10^{-68}}\right]^{3/2} = 8.373 \times 7.055 \times 10^{27}$$

$$\Rightarrow n = 59.071515 \times 10^{27} \text{ per m}^3$$

$$\Rightarrow \boxed{n = 5.9 \times 10^{28} \text{ per m}^3}.$$

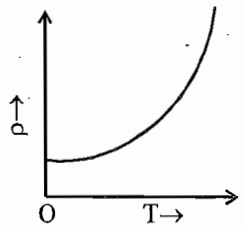
Hence, correct answer is (5.9).

PRACTICE SET

1. Na metal with bcc structure has radius of Na atom to be 1.85Å. Calculate
   (a) Fermi energy
   (b) Electrical resistivity from a Drude model (Relaxation time $\tau = 3\times10^{-14}$ sec)

2. Specific heat at low temperature is dominated by
   (a) core electron (b) conduction electron
   (c) lattice vibration (d) none of these

3. Graph shown is for
   (a) semiconductor
   (b) metal
   (c) superconductor
   (d) none of these



4. If the Fermi energy of a metal at 0°K, 10 eV, the mean energy of the electrons in the metal at 0 K is
   (a) 6 eV (b) 5 eV (c) 1.5 e V (d) 2 eV

5. The Fermi energy of silver is 5.51 electron volt. The average energy of the free electrons in silver at 0° K is given by
   (a) 4.205 eV (b) 0.864 eV (c) 3.306 eV (d) 9.425 eV

6. If the number of quantum states $g(\varepsilon)\,d\varepsilon$ available to to electron in a metal with energies between ε and $\varepsilon + d\varepsilon$ is $g(\varepsilon)\,d\varepsilon = \left(\frac{3N}{2}\right)\varepsilon_f^{-3/2}\sqrt{\varepsilon}\,d\varepsilon$, where ε_f Fermi energy and N is the number of electrons present then the average electron energy at $T = 0°\,K$ is
   (a) $\frac{3}{5}\varepsilon_f$ (b) $\frac{1}{5}\varepsilon_f$ (c) $\frac{2}{5}\varepsilon_f$ (d) ε_f

7. For one dimensional crystal, the average kinetic energy in the ground state is
   (a) $\frac{1}{2}E_F$ (b) $\frac{1}{3}E_F$ (c) $\frac{3}{5}E_F$ (d) $\frac{2}{3}E_F$

8. The crystal A in the wave function of one-dimensional free electrons gas is given by
   (a) $\sqrt{\frac{1}{L}}$ (b) $\sqrt{\frac{2}{L}}$ (c) $\sqrt{\frac{3}{L}}$ (d) $\sqrt{\frac{4}{L}}$

9. The lowest energy of an electron confined to move in a one dimensional potential well of length 0.5 Å is
   (a) 150.7 eV (b) 250.7 eV (c) 350.7 eV (d) 450.7 eV

10. The lowest energy of a neutron of mass 1.6×10^{-27} kg confined to a nucleus of size 10^{-14} cm is
    (a) 2.14×10^4 eV (b) 2.14×10^6 eV (c) 2.14×10^8 eV (d) 2.14×10^{10} eV

11. An electron is made to confine in a one dimensional potential well. If its energy in the 5th quantum state is 230 eV, the width of the potential well is
    (a) 2.02 Å (b) 3.02 Å (c) 4.02 Å (d) 5.02 Å

12. The lowest permissible quantum state energy for an electron confined in a box of side 2 Å is
    (a) 18.27 eV (b) 28.27 eV (c) 38.27 eV (d) 48.27 eV

13. The atomic radius of sodium is 1.86 Å. Calculate the Fermi energy of sodium at absolute zero.

14. Calculate the Fermi energy of electrons at 0K for a metal with electron density of 10^{28} m^{-3}.

15. Silver (fcc) has an atomic radius of 1.44 Å. Assuming silver to be monovalent metal. calculate the value of the Fermi energy, the Fermi temperature and the Fermi velocity.

16. Aluminium metal crystallises in fcc structure. If each atom contributes single electron as free electron and the lattice constant is 4Å, calculate (treating conduction electron as free electron Fermi gas)
    (i) Fermi energy (E_F) and the Fermi energy wave vector (k_F),
    (ii) Total kinetic energy of free electron gas per unit volume at 0 K.
    Given $\hbar = 1.054 \times 10^{-27}$ erg-s; Electron rest mass = 9.11×10^{-28}g.

17. The density of potassium is 860 kgm^{-3}. Calculate the Fermi energy and compressibility of potassium at 0 K. (Atomic mass of K = 39.1 amu).

18. If Fermi temperature is of the order of 5×10^4 K, provide a rough estimate of electronic specific heat at 100K.

ANSWER KEY

1. (3.15 eV, 4.61×10^{-8} Ω-m) 2. (b) 3. (b) 4. (a)

5. (c) 6. (a) 7. (b) 8. (b) 9. (a) 10. (b)

11. (a) 12. (b) 13. (3.11 eV) 14. (1.69 eV)

15. (5.50 eV, 63850 K, 1.39×10^6 ms^{-1})

16. (2.28 eV, 7.73×10^9 m^{-1}, 2.14×10^{28} eVm^{-3})

17. (2.02 eV, 3.51×10^{-10} N^{-1}m^2)

18. (>> 0.025 J)

Chapter 7

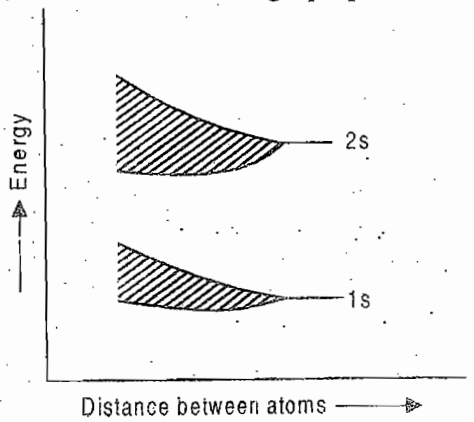
BAND THEORY OF SOLIDS

Periodic potential in a crystalline solid :

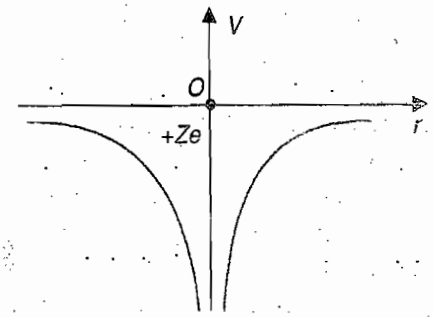
Consider an electron in the vicinity of an atomic nucleus of charge Ze. The potential energy of the electron in S.I. units is given by

$$V = -\frac{Ze^2}{4\pi\varepsilon_0 r} \qquad \ldots (1)$$

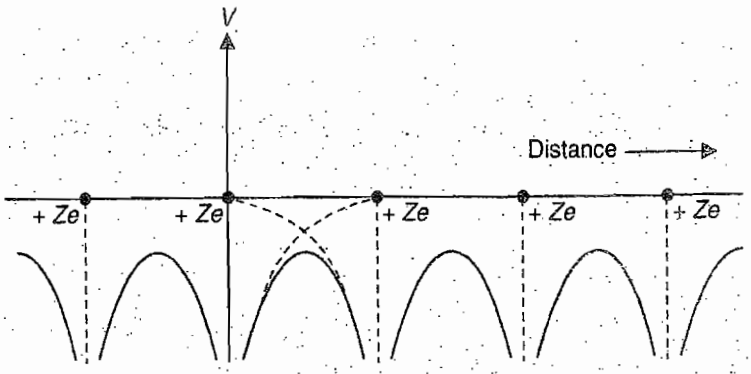
where, ε_0 is the free-space permitivity and r is the distance of the electron from the nucleus. The variation of the potential energy with the distance r is shown in figure. When a number of such atomic nuclei are brought close together to form a crystal, the potential energy of an electron is obtained by summing up the potential energies due to the individual nuclei. Thus the potential energy as a function of distance for an infinite one-dimensional crystal would be as shown in figure. Note that the potential energy is a periodic function of distance, the atomic nuclei being equispaced.



Formation of bands for 1s and 2s states.



Variation of potential energy with distance for an isolated atom.



Variation of potential energy with distance for a one-dimensional crystal

The Kronig-Penney model :

In this model, for the sake of convenience, the periodic potential energy curve is approximated by square wells as shown in figure . Let the period of the periodic potential be $(a+b)$.

For, $-b<x<0$, the potential energy is V_0 while for $0<x<a$, the potential energy is zero. The Schrodinger equations are

$$\frac{d^2\psi}{dx^2}+\frac{2m}{\hbar^2}E\psi=0 \qquad \text{for } 0<x<a \qquad \ldots(2)$$

$$\Rightarrow \quad \frac{d^2\psi}{dx^2}+\frac{2m}{\hbar^2}(E-V_0)\psi=0 \qquad \text{for } -b<x<0 \qquad \ldots(3)$$

Assuming that the electron energy E is less than V_0. Let

$$\alpha^2=\frac{2mE}{\hbar^2} \quad \text{and} \quad \beta^2=\frac{2m}{\hbar^2}(V_0-E) \qquad \ldots(4)$$

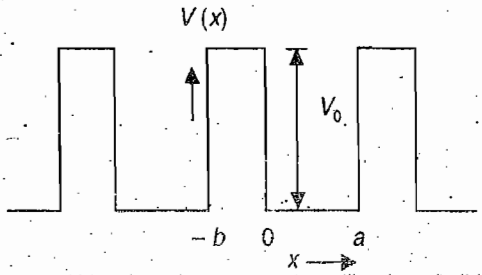
Then equations (2) and (3) become

$$\frac{d^2\psi}{dx^2}+\alpha^2\psi=0 \qquad \text{for } 0<x<a \qquad \ldots(5)$$

$$\Rightarrow \quad \frac{d^2\psi}{dx^2}-\beta^2\psi=0 \qquad \text{for } -b<x<0 \qquad \ldots(6)$$

Since, the potential is periodic, i.e.,

$$V(x)=V(x+a+b) \qquad \ldots(7)$$



The Kroning-Penney model potential

Bloch's theorem states that for a periodic potential of the form of equation (7), the solution of the Schrodinger equations are of the form

$$\psi=u_k(x)\exp(ikx) \qquad \ldots(8)$$

where $u_k(x)$ is a periodic function with the periodicity of lattice, i.e.,

$$u_k(x)=u_k(x+a+b) \qquad \ldots(9)$$

Wave functions of the form of equation (9) are called **Bloch functions**. Substituting equation (8) into equations (2) and (3), we obtain

$$\frac{d^2u}{dx^2}+2ik\frac{du}{dx}+(\alpha^2-k^2)u=0, \qquad 0<x<a \qquad \ldots(10)$$

$$\Rightarrow \quad \frac{d^2u}{dx^2}+2ik\frac{du}{dx}-(\beta^2+k^2)u=0, \qquad -b<x<0 \qquad \ldots(11)$$

The solutions of equations (10) and (11) are

$$u_1 = A\exp\left[i(\alpha - k)x\right] + B\exp\left[-i(\alpha + k)x\right], \qquad 0 < x < a \qquad \ldots (12)$$

$$u_2 = C\exp\left[(\beta - ik)x\right] + D\exp\left[-(\beta + ik)x\right], \qquad -b < x < 0 \qquad \ldots (13)$$

where A, B, C and D are constants. These constants are determined in such a way that the wave function ψ and its normal derivative $d\psi/dx$ are single-valued and continuous. That is,

$$u_1(0) = u_2(0), u_1(a) = u_2(-b),$$

$$\left(\frac{du_1}{dx}\right)_{x=0} = \left(\frac{du_2}{dx}\right)_{x=0} \Rightarrow \left(\frac{du_1}{dx}\right)_{x=a} = \left(\frac{du_2}{dx}\right)_{x=-b} \qquad \ldots (14)$$

Using these conditions in equations (12) and (13), we get

$$A + B = C + D \qquad \ldots (15)$$

$$i(\alpha - k)A - i(\alpha + k)B = (\beta - ik)C - (\beta + ik)D \qquad \ldots (16)$$

$$A\exp\left[i(\alpha - k)a\right] + B\exp\left[-i(\alpha + k)a\right] = C\exp\left[-(\beta - ik)b\right] + D\exp\left[(\beta + ik)b\right] \qquad \ldots (17)$$

$$\Rightarrow i(\alpha - k)A\exp\left[i(\alpha - k)a\right] - i(\alpha + k)B\exp\left[(\beta + ik)b\right]$$

$$= (\beta ik)C\exp\left[-(\beta - ik)b\right] - i(\beta + ik)D\exp\left[(\beta + ik)b\right] \qquad \ldots (18)$$

Equations (15) through (18) are homogeneous and will have a solution other than $A = B = C = D = 0$, provided the determinant of the coefficients A, B, C and D vanishes. Expanding this determinant and simplifying, we obtain.

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta}\sin\beta b \sin\alpha a + \cosh\beta b \cos\alpha a = \cos k(a + b) \qquad \ldots (19)$$

From $E > V_0$, β imaginary. For such energies we put $\beta = i\gamma$ and note that $\sinh i\gamma b = i\sin\gamma b$ and $\cosh i\gamma b = \cos\gamma b$. Then we obtain from equation (19)

$$-\frac{\alpha^2 + \gamma^2}{2\alpha\gamma}\sin\gamma b \sin\alpha a + \cos\gamma b \cos\alpha a = \cos k(a + b) \qquad \ldots (20)$$

It is convenient to use equation (19) when $0 < E < V_0$ and equation (20) when $E > V_0$. Equations (19) and (20) may also be written respectively in the forms.

$$\left[1 + \frac{(\beta^2 + \alpha^2)^2}{4\alpha^2\beta^2}\sin^2\beta b\right]^{1/2}\cos(\alpha a - \theta) = \cos k(a + b) \qquad \ldots (21)$$

where, $\tan\theta = \frac{\beta^2 - \alpha^2}{2\alpha\beta}\tanh\beta b,$

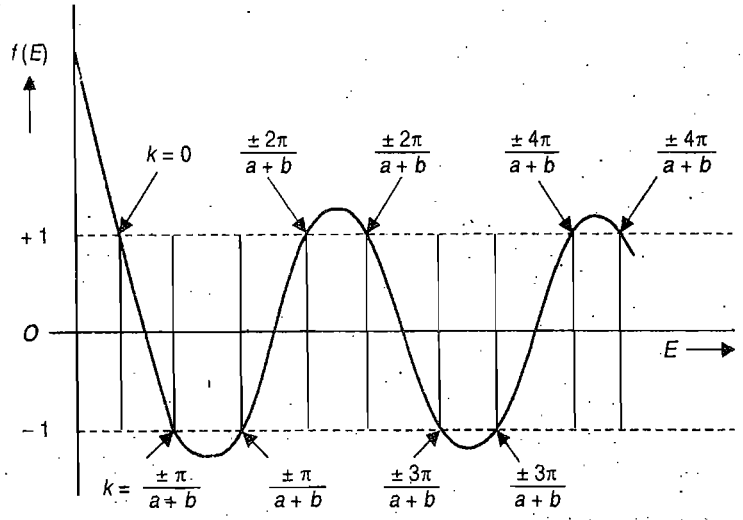
$$\Rightarrow \left[1 + \frac{(\alpha^2 - \gamma^2)^2}{4\alpha^2\gamma^2}\sin^2\gamma b\right]\cos(\alpha a - \theta) = \cos l(a + b) \qquad \ldots (23)$$

where $\tan\theta = -\frac{\alpha^2 + \gamma^2}{2\alpha\gamma}\tan\gamma b$

In equations (19) and (20) the left-hand sides are cosine functions multiplied by factors which are greater than

unity. The multiplying factor is a maximum for $\alpha = 0$, i.e. for $E = 0$, and approaches unity for large energies when $\alpha^2 = -\beta^2$

Equations (19) and (20) are transcendental in nature and may be solved graphically. The left-hand side of either of these equations is plotted as a function of E in figure below. The right-hand side of each equation is $\cos k(a+b)$ which lies between +1 and –1. Thus physically acceptable solutions are possible when the left-hand side of equations (19) or (20) lies between +1 and –1. The corresponding energy values are permitted. Outside these limits, physical solutions are not possible and the corresponding energies are forbidden. Thus, allowed and forbidden energy bands are alternately produced. The forbidden energy bands are shown as shaded regions in figure below



With the help of above figure, i.e. equation (19) and (20), one can plot the energy E as a function of the wave vector k. Such a plot is shown in figure. The edges of the allowed bands occur when $\cos k(a+b) = \pm 1$, i.e. when $k = \pm \frac{n\pi}{a+b}$, where n is zero or an integer. The E-k diagram has the following important features:

(i) As $E \to \infty$, the E-k relationship approaches that for a free electron; i.e. we have $E = \hbar^2 k^2 / 2m_0$ which is shown as a dotted curve in figure.

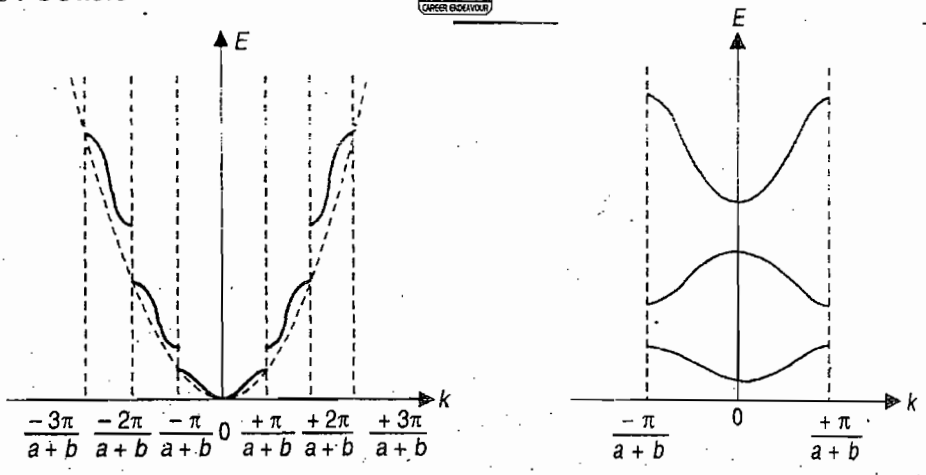
(ii) For large energies, the allowed bands are broad and the forbidden bands are narrow.

(iii) If the wells are deep and widely spaced, i.e. if b and V_0 are large, a low energy electron will be practically bound to one of the wells. Thus the low energy eigenvalues will be nearly equal to those of a single well. If the wells are close together, the levels spread into energy bands. As the separation b is reduced, the allowed bands become wider.

(iv) As the barrier height V_0 is increased with a and b remaining fixed, the widths of the energy bands decrease.

(v) At the edges of the allowed bands, i.e. at $k = \pm \frac{n\pi}{a+b}$, the slope of the E-k curve is zero.

Reduced Zone representation:



Extended zone scheme Reduced zone scheme

In figure above the region extending from $k=-\frac{\pi}{a+b}$ to $k=\frac{\pi}{a+b}$ is called the first Brillouin zone, that from $-2\pi/(a+b)$ to $-\pi/(a+b)$ and from $\pi/(a+b)$ to $2\pi/(a+b)$ is known as the second Brillouin zene, and so on. In equations (19) and (20) if k is replaced by $k+\left[2n\pi/(a+b)\right]$ where n is an integer, positive or negative, the equations are still satisfied since such replacements do not alter the value of $\cos k(a+b)$. Thus k is not uniquely determined, and it is often very userful to translate the various segments of the E-k curve in figure parallel to the k-axis through distances that are integral multiples of $2\pi/(a+b)$ so that k lies within the region $-\pi/(a+b)\le k\le\pi/(a+b)$. The resulting representation of the E-k diagram, shown in figure, is referred to as the reduced zone representation.

The E-k curve in the extended zone scheme is figure above has discontinuities at $k=n\pi/(a+b)$ where $n=\pm1,\pm2,$ etc. These k-values give the boundaries of the Brillouin zone. As $k=2\pi/\lambda$, the Brillouin zone boundaries are defined in terms of λ by $2(a+b)=n\lambda$, which is Bragg's law of reflection for normal incidence. Thus the discontinuitites in the E-k curves are associated with the Bragg reflection of the de-Broglie waves representing the electrons for these k-values.

Effective mass of electron:

It is known that electron has a well defined mass and when accelerated by an electric field, it obeys Newtonian mechanics. What happens when the electron is to be accelerated inside a crystal? How will it react to an electric field? The mass of an electron in a crystal appears, in general different from the electron mass and is usually referred to as the effective mass. The velocity of the electron in a one dimensional lattice is described by its group velocity given by the equation.

$$v=\frac{d\omega}{dk}\Rightarrow v=\frac{1}{\hbar}\frac{dE}{dk} \qquad \ldots(1)$$

$$\therefore \quad \text{acceleration } a=\frac{dv}{dt}=\frac{1}{\hbar}\frac{d}{dt}\left(\frac{dE}{dk}\right)=\frac{1}{\hbar}\frac{d}{dk}\left(\frac{dE}{dk}\right)\frac{dk}{dt}$$

$$\Rightarrow \quad a=\frac{1}{\hbar}\frac{d^2E}{dk^2}\frac{dk}{dt} \qquad \ldots(2)$$

Now we will find the value of $\frac{dk}{dt}$ under the influence of an applied field E.

Let an electron be subjected to the influence of an external field of strength $\mathcal{E}$ for a time dt. If the velocity of the electron is v, the distance travelled in a time dt is vdt.

So, that

$$dE = e\,\mathcal{E}\,v dt \Rightarrow dE = e\,\mathcal{E}\,\frac{1}{\hbar}\left(\frac{dE}{dk}\right)dt$$

$$\Rightarrow \qquad \frac{dk}{dt} = \frac{e\mathcal{E}}{\hbar} \qquad \ldots (3)$$

Putting (3) in equation (2) we get

$$a = \frac{1}{\hbar}\frac{d^2E}{dk^2}\left(\frac{e\mathcal{E}}{\hbar}\right) \qquad \Rightarrow \qquad a = \frac{1}{\hbar^2}e\mathcal{E}\left[\frac{d^2E}{dk^2}\right] \qquad \ldots (4)$$

Compering this formula with that for a free, classical particle,

$$m\left(\frac{du}{dt}\right) = e\mathcal{E} \Rightarrow \qquad \frac{dv}{dt} = a = \frac{e\mathcal{E}}{m} \qquad \ldots (5)$$

$\therefore$ From equations (4) and (5), we get

$$\text{effective mass } (m^*) = \frac{\hbar^2}{\left(\frac{d^2E}{dk^2}\right)} \qquad \ldots (6)$$

So as to write in all case,

$$a = \frac{e\,\mathcal{E}}{m^*} \qquad \ldots (7)$$

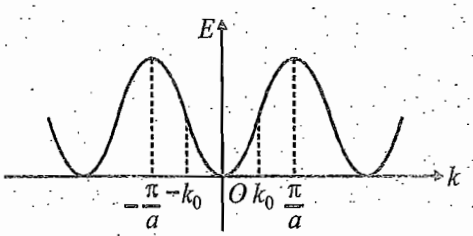
So, equation (6) indicate, that the effective mass is determined by $\frac{d^2E}{dk^2}$. It can be shown that for a free electron $m^* = m$ because $E = \frac{\hbar^2k^2}{2m}$ and $m^* = \frac{\hbar^2}{d^2E/dk^2}$.

But for an electron moving in a periodic potential, E does not vary with k in the above manner (i.e. curve E versus k is not a parabolic) and So, $m^* \neq m$. So, we can conclude that all the results of the free electron theory are those provided in m in each case is replaced by suitable m^*. Thus

$$E = \frac{\hbar^2k^2}{2m^*}$$

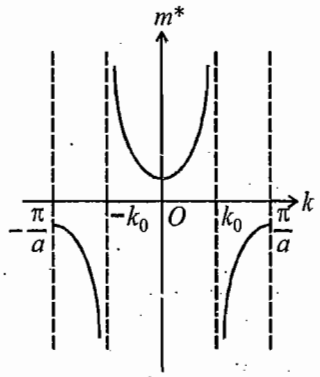
This is known as effective mass approximation.

Variation of effective mass (m^*) with k:



at $k = 0$, E is minimum $\Rightarrow$ $\frac{d^2E}{dk^2}$ = positive $\Rightarrow$ m^* = positive (finite)

at $k = \pm\frac{\pi}{a}$, E is maximum $\Rightarrow$ $\frac{d^2E}{dk^2}$ = negative $\Rightarrow$ m^* = negative



SOLVED PROBLEMS

1. Taking the origin at the bottom of the conduction band, calculate the crystal momentum for a free electron of energy 0.02 eV. Given, effective mass of the electron = $0.2\,m_0$.

Soln. Taking the origin at the bottom of the conduction band, the energy (E) versus the wave vector (k) relationship is $E = \frac{\hbar^2 k^2}{2m^*}$.

Here, $E = 0.02$ eV $= 0.02\times1.6\times10^{-19}$ J and $m^* = 0.2\,m_0 = 0.2\times9.11\times10^{-31}$ kg

Hence, crystal momentum $= \hbar k = \left(2m^*E\right)^{1/2} = \left(2\times0.2\times9.11\times10^{-31}\times0.02\times1.6\times10^{-19}\right)^{1/2}$

$= 3.416\times10^{-26}$ kg.m/s

2. The intrinsic carrier concentration of germanium at room temperature is 2.5×10^{19} m^{-3}. It is doped with phosphorus at a rate of 1 phosphorus atom per million atoms of germanium. If the concentration of germanium. If the concentration of germanium atoms is 5×10^{28} m^{-3}, calculate the hole concentration. Assume complete ionization of phosphorus atoms.

Soln. The number of phosphorus atoms $= \frac{5\times10^{28}}{10^6}$ m^{-3} $= 5\times10^{22}$ m^{-3}. For complete ionization, the concentration of electrons is $n = 5\times10^{22}$ m^{-3}.

We have $np = n_i^2$ where n_i is the intrinsic carrier concentration. Therefore, the hole concentration,

$$p = \frac{n_i^2}{n} = \frac{\left(2.5\times10^{19}\right)^2}{5\times10^{22}}\text{ m}^{-3} = 1.25\times10^{16}\text{ m}^{-3}$$

3. Show that the fractional increase in the intrinsic carrier concentration of Si at room temperature increases by 8% per degree rise of temperature.

Soln. The intrinsic carrier concentration is given by

$$n_i = CT^{3/2}\,e^{-E_g/(2k_BT)} \qquad \text{... (i)}$$

where C is a constant. The band gap E_g decreases linearly with temperature obeying the relationship $E_g = E_{g_0} - \alpha T$, where E_{g_0} is the energy gap at 0 K. Substituting this relationship into equation (i), we obtain

$$n_i = C' T^{3/2} e^{-E_{g_0}/(2k_B T)} \qquad \text{... (ii)}$$

where C' is a new constant. Logarithmic differentiation of equation (ii) shows that the fractional increase in n_i is given by

$$\frac{\delta_{n_i}}{n_i} = \left(\frac{3}{2} + \frac{E_{g_0}}{2k_B T}\right)\frac{\delta T}{T}$$

For Si, $E_{g_0} = 1.21$ eV. At room temperature ($T = 300$ K), we have $k_B T = 26$ meV $= 26 \times 10^{-3}$ eV. So, for Si at 300 K with $\delta T = 1$ K, we obtain

$$\frac{\partial n_i}{n_i} = \left(\frac{3}{2} + \frac{1.21}{0.052}\right)\frac{100}{300}\% = 8\%$$

4. Silicon contains 5×10^{28} atoms per m^3. In an n-type Si sample and the donor concentration is 1 atom per 2.5×10^7 Si atoms. Assuming that the electron effective mass is equal to the true mass, calculate the temperature at which the Fermi level lies at the bottom of the conduction band.

Soln. The donor concentration $N_D = \dfrac{5 \times 10^{28}}{2.5 \times 10^7} = 2 \times 10^{21}$ m^{-3}

Also, $n_0 = 4.82 \times \left(\dfrac{m_e}{m_0}\right)^{3/2} T^{3/2} = 4.82 \times 10^{21}\, T^{3/2}$ (Since, $m_e = m_0$).

The fermi level is $E_F = E_C - k_B T \ell n \left(\dfrac{n_C}{n_D}\right)$.

Since, $T \neq 0$, $E_F = E_C$ when $n_C = N_D$, i.e.,

$$4.82 \times 10^{21}\, T^{3/2} = 2 \times 10^{21}$$

whence, $T = 0.56$ K

5. The energy wave vector dispersion relation for a one-dimensional crystal of lattice constant a is given by $E(k) = E_0 - \alpha - 2\beta \cos ka$, where E_0, α, β are constants.

(i) Find the value of k at which the velocity of an eelctron is a maximum.
(ii) Find the difference between the top and the bottom of the energy band.
(iii) Obtain the effective mass m^* of the electron at the bottom and at the top of the band.

Soln. (i) The velocity of an electron is $v = \dfrac{1}{\hbar}\dfrac{dE}{dk} = \dfrac{2\beta a}{\hbar}\sin ka$

v is maximum when $\sin ka = 1 \Rightarrow ka = \dfrac{\pi}{2} \Rightarrow k = \dfrac{\pi}{2a}$

(ii) At the top of the band $E(k)$ is a maximum, and so cos ka is a minimum, i.e. cos $ka = -1$.

So, $E_{top} = E_0 - \alpha + 2\beta$

At the bottom of the band $E(k)$ is a minimum, i.e. cos ka attains a maximum value of +1. Hence

$$E_{bot} = E_0 - \alpha - 2\beta$$

The difference in energy is, $E_g = E_{top.} - E_{bot} = 4\beta$

(iii) $m^* = \dfrac{\hbar^2}{d^2E/dk^2} = \dfrac{\hbar^2}{2\beta a^2 \cos ka}$

At the bottom of the band, $\cos ka = 1$; so $m^* = \dfrac{\hbar^2}{2\beta a^2}$

At the top of the band, $\cos ka = -1$; so $m^* = -\dfrac{\hbar^2}{2\beta a^2}$

6. The concentration of ionized donor and acceptors in an n-type compensated semiconductor at temperature T are N_D and N_A respectively. If n_i is the intrinsic carrier concenration at that temperature, show that the concentration of free electrons and holes in the semiconductor are

$$n = \frac{1}{2}(N_D - N_A) + \frac{1}{2}\sqrt{(N_D - N_A)^2 + 4n_i^2}$$

and $$p = -\frac{1}{2}(N_D - N_A) + \frac{1}{2}\sqrt{(N_D - N_A)^2 + 4n_i^2}$$ respectively.

Soln. As the semiconductor is electrically neutral, we have

$$N_D + p = N_A + n \qquad \ldots \text{(i)}$$

For an n-type semiconductor, $N_D > N_A$. Also, $p = \dfrac{n_i^2}{n}$, so, equation (i) becomes.

$$N_D + \frac{n_i^2}{n} = N_A + n \;\Rightarrow\; n^2 - (N_D - N_A)n - n_i^2 = 0$$

$$\Rightarrow \qquad n = \frac{1}{2}(N_D - N_A) \pm \frac{1}{2}\sqrt{(N_D - N_A)^2 + 4n_i^2}$$

Since n is positive, the negative sign on the right-hand side must be rejected. Hence

$$n = \frac{1}{2}(N_D - N_A) + \frac{1}{2}\sqrt{(N_D - N_A)^2 + 4n_i^2},$$

Similarly, putting $n = n_i^2/p$ on the right-hand side of equation (i) and proceeding in the same way, we obtain

$$p = -\frac{1}{2}(N_D - N_A) + \frac{1}{2}\sqrt{(N_D - N_A)^2 + 4n_i^2}$$

7. For a solid tight bonding approximation expression is given by

$$E(k) = E_0 - C\cos(k_x a)\cos(k_y a)$$

(a) Expand $E(k)$ (b) band-width of the band

(c) Density of states near (0, 0) (d) Effective mass at $(0, \pi/a)$ and (0, 0)

Soln: $E = E_0 - C\cos(k_x a)\cos(k_y a)$.

Lattice parameter = $2a$

For rhombic dodecahedron, (for FCC to BCC)

top of band from cubic $\left(\frac{2\pi}{a},0,0\right)\Big/\left(0,\frac{2\pi}{a},0\right)\Big/\left(0,0,\frac{2\pi}{a}\right)$, when lattice parameter is a.

For $2-D$, $(\pi/a, 0)$ or $(0, \pi/a)$ top of band

(a) $E = E_0 - C$

(b) $E_{top} = E_0 - C$ at $\left(\frac{\pi}{a},0\right)$ $\qquad E_{bottom} = E_0 - C$ at $(0, 0)$

Therefore, band-width, $E_g = 2C$

(c) $E = E_0 - C\left\{\left[1-\frac{k_x^2a^2}{2}\right]\left[1-\frac{k_y^2a^2}{2}\right]\right\} = E_0 - C\left[1-\frac{k_y^2a^2}{2}-\frac{k_x^2a^2}{2}+\frac{k_x^2k_y^2a^4}{4}\right]$ near $(0, 0)$

$= E_0 - C\left[1-\frac{1}{2}a^2\left(k_x^2+k_y^2\right)\right] = E_0 - C\left[1-\frac{k^2a^2}{2}\right] = E_0 - C + C\frac{k^2a^2}{2} \quad \Rightarrow \frac{dE}{dk} = Ca^2k$

$\therefore \qquad D(E) = 2\left(\frac{L}{2\pi}\right)^2 \frac{1}{Ca^2k} = \frac{2L^2}{4\pi^2Ca^2k} = \frac{A}{2\pi^2a^2Ck}$

(d) $m^*(0, \pi/2)$ = top of bond

$\Rightarrow \qquad \frac{d^2E}{dk^2} = Ca^2$

Therefore, m^* at top $= \frac{-\hbar^2}{Ca^2}$ and $m^*(0, 0) = \frac{\hbar^2}{Ca^2}$

8. The energy bond relation in a linear chain with interatomic distance a is given by.

$$E(k) = E_0 - T\cos ka$$

When width of this bond is increased by 20%, calculate the % change in the effective mass of the electron at the bottom of the band.

Soln. $E(k) = E_0 - T\cos ka$

$v_g = \frac{1}{\hbar}\frac{dE}{dk} = \frac{Ta\sin ka}{\hbar}$

$D(E) = 2\times\frac{L}{2\lambda Ta\sin ka} = \frac{L}{T\pi a\sin ka}$

and $\frac{d^2E}{dk^2} = Ta^2\cos ka \Rightarrow m^* = \frac{\hbar^2}{Ta^2\cos ka}$

$E_{top} = E_0 + T$ and $E_{bottom} = E_0 - T$

$\therefore \Delta E = 2T$.

$$m^* = \frac{2\hbar^2}{\Delta E\, a^2\, ka}$$

$$\Rightarrow \ell n\, m^* = \ell n 2 + \ell n\, \hbar^2 - \ell n(\Delta E) - \ell n(a^2) - \ell n(\cos ka)$$

$$\Rightarrow \frac{1}{m^*} dm^* = 0 + 0 - \frac{1}{\Delta E} d(\Delta E) - 0 - 0 \Rightarrow \frac{dm^*}{m^*} = -\frac{d(\Delta E)}{\Delta E}$$

$$\Rightarrow \frac{dm^*}{m^*} \times 100 = \frac{d(\Delta E)}{\Delta E} \times 100 \Rightarrow \frac{dm^*}{m^*} \times 100 = 20\%$$

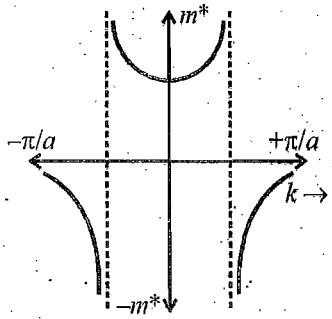
i.e., band width increases 20%, m^* decreases by 20%.

9. In a one-dimensional Kronig-Penney model, the total number of possible wave function is equal to
(a) twice the number of unit cells (b) number of unit cells **[GATE 2002]**
(c) half the number of unit cells (d) independent of the number of unit cells

Soln. For one dimensional Kronig Penney model, total number of wave function is equal to the number of unit cells.
Hence, correct option is (b).

10. The effective mass of an electron in a semiconductor can be **[GATE 2003]**
(a) negative near the bottom of the end. (b) a scalar quantity with a small magnitude.
(c) zero at the center of the band. (d) negative near the top of the band.

Soln. The effective mass (m^*) can be represented as:



From this figure, it is clear that m^* is negative near the top of the band.
Hence, correct option is (a).

11. Consider the energy E in the first Brillouin zone as a function of the magnitude of the wave vector k for a crystal of lattice constant a. Then, **[GATE 2003]**

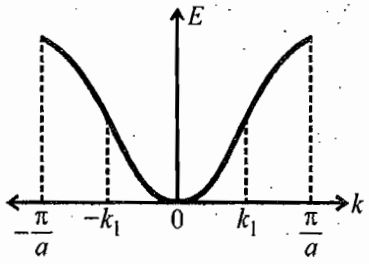
(a) the slope of E versus k is proportional to the group velocity.

(b) the slope of E versus k has its maximum value at $|k| = \frac{\pi}{a}$.

(c) the plot of E versus k will be parabolic in the inteval $\left(-\frac{\pi}{a}\right) < k < \left(\frac{\pi}{a}\right)$.

(d) the slope of E versus k is non zero for all k in the interval $\left(-\frac{\pi}{a}\right) < k < \left(\frac{\pi}{a}\right)$.

Soln. E-k diagram is represented in the figure. Also it is expressed as $E = \dfrac{\hbar^2 k^2}{2m}$ ... (i)



It is clear from equation (i) that the plot of E versus k will be parabolic in the interval $\left(-\dfrac{\pi}{a}\right) < k < \left(\dfrac{\pi}{a}\right)$.

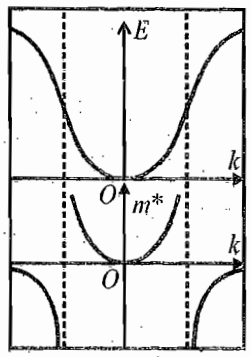
Hence, correct option is (c).

12. The effective mass of an electron in a semiconductor **[GATE 2004]**

(a) can never be positive (b) can never be negative
(c) can be positive or negative (d) depends on its spin

Soln. An electron moving in a crystal has an effective mass m^*,

$$m^* = \frac{\hbar^2}{\left(\dfrac{d^2E}{dk^2}\right)}$$



$\Rightarrow$ m^* can be positive in the lower half of the energy band and negative in the upper half.

Hence, correct option is (c).

13. The energy $E(\vec{k})$ of electrons of wave vectors $\vec{k}$ in a solid is given by $E(\vec{k}) = Ak^2 + Bk^4$, where A and B are constants. The effective mass of the electron at $k = k_0$ is **[GATE 2006]**

(a) Ak_0^2 (b) $\dfrac{\hbar^2}{2A}$ (c) $\dfrac{\hbar^2}{(2A + 12Bk_0^2)}$ (d) $\dfrac{\hbar^2}{Bk_0^2}$

Soln. Effective mass $(m^*) = \dfrac{\hbar^2}{\left(\dfrac{d^2E}{dk^2}\right)}$ ... (i)

Here, $E(\vec{k}) = Ak^2 + Bk^4$

$$\frac{dE}{dk} = 2Ak + 4Bk^3 \; ; \; \frac{d^2E}{dk^2} = 2A + 12Bk^2$$

At $k = k_0$, $\left.\dfrac{d^2E}{dk^2}\right|_{k=k_0} = 2A + 12Bk_0^2$ ... (ii)

From equation (ii), equation (i) implies $m^* = \dfrac{\hbar^2}{(2A + 12Bk_0^2)}$.

Hence, correct option is (c).

14. If the number density of a free electron gas changes from 10^{28} to 10^{26} electron/m^3, the value of plasma frequency (in Hz) changes from 5.7×10^{15} to **[GATE 2006]**

(a) 5.7×10^{13} (b) 5.7×10^{14} (c) 5.7×10^{16} (d) 5.7×10^{7}

Soln. The plasma frequency (ω_p) is directly proportional to density of free electrons

i.e., $\omega_p \propto \sqrt{N}$ ... (i)

Initially the electron density, $N_1 = 10^{28}$ electrons/m^3

Finally the electron density, $N_2 = 10^{26}$ electrons/m^3 and initial plasma frequency $(\omega_p)_1 = 5.7 \times 10^{15}$ Hz.

Let the final plasma frequency $(\omega_p)_2 = x$

$$\therefore \quad \frac{(\omega_p)_1}{(\omega_p)_2} = \sqrt{\frac{N_1}{N_2}} = \sqrt{\frac{10^{28}}{10^{26}}} \quad \Rightarrow \quad \frac{5.7 \times 10^{15}}{x} = \sqrt{\frac{10^{28}}{10^{26}}}$$

$$\Rightarrow \quad x = 5.7 \times 10^{15} \times \sqrt{\frac{10^{26}}{10^{28}}} = 5.7 \times 10^{15} \times \left(\frac{1}{10}\right) \quad \Rightarrow \quad x = 5.7 \times 10^{14} \text{ Hz}$$

Hence, correct option is (b).

15. An electron of wavevector $\vec{k_e}$, velocity $\vec{v_e}$ and effective mass m_e is removed from a filled energy band. The resulting hole has wavevector $\vec{k_h}$, velocity $\vec{v_h}$, and effective mass m_h. Which one of the following statements is correct ? **[GATE 2009]**

(a) $\vec{k_h} = -\vec{k_e}\,;\ \vec{v_h} = -\vec{v_e}\,;\ m_h = -m_e$ (b) $\vec{k_h} = -\vec{k_e}\,;\ \vec{v_h} = \vec{v_e}\,;\ m_h = m_e$

(c) $\vec{k_h} = -\vec{k_e}\,;\ v_h = -\vec{v_e}\,;\ m_h = -m_e$ (d) $\vec{k_h} = -\vec{k_e}\,;\ \vec{v_h} = -\vec{v_e}\,;\ m_h = -m_e$

Soln. For hole, $\vec{k_h} = -\vec{k_e}$, $\vec{v_h} = -\vec{v_e}$ and $m_h = -m_e$

These relations are obtained by using mass and momentum conservation laws.

Hence, correct option is (a).

16. The Bloch theorem states that within a crystal, the wave function $\psi(\vec{r})$, of an electron has the form

(a) $\psi(\vec{r}) = u(\vec{r})\, e^{i\vec{k}\cdot\vec{r}}$, where $u(\vec{r})$ is an arbitrary function and $\vec{k}$ is an arbitrary vector. **[GATE 2010]**

(b) $\psi(\vec{r}) = u(\vec{r})\, e^{i\vec{G}\cdot\vec{r}}$, where $u(\vec{r})$ is an arbitrary function and $\vec{G}$ is a reciprocal lattice vector.

(c) $\psi(\vec{r}) = u(\vec{r})\, e^{i\vec{G}\cdot\vec{r}}$, where $u(\vec{r}) = u(\vec{r} + \vec{A})$, $\vec{A}$ is a lattice vector and $\vec{G}$ is a reciprocal lattice vector.

(d) $\psi(\vec{r}) = u(\vec{r})\, e^{i\vec{k}\cdot\vec{r}}$, where $u(\vec{r}) = u(\vec{r} + \vec{A})$, $\vec{A}$ is a lattice vector and $\vec{k}$ is an arbitrary vector.

Soln. Option (d) is the correct statement of Bloch theorem.

Hence, correct option is (d).

17. The tight binding energy distribution $(E - k)$ relation for electrons in a one-dimensional array of atoms having lattice constant a and total length L **[GATE 2011]**

$E = E_0 - \beta - 2\gamma \cos(ka)$, where E_0, β and γ are constants and k is the wavevector.

(A) The density of state of electrons (including spin degeneracy) in the band is given by

(a) $\dfrac{L}{\pi \gamma a \sin(ka)}$ (b) $\dfrac{L}{2\pi \gamma a \sin(ka)}$ (c) $\dfrac{L}{2\pi \gamma a \cos(ka)}$ (d) $\dfrac{L}{\pi \gamma a \cos(ka)}$

(B) The effective mass of electrons in the band is given by

(a) $\frac{\hbar^2}{\gamma a^2 \cos(ka)}$ (b) $\frac{\hbar^2}{2\gamma a^2 \cos(ka)}$ (c) $\frac{\hbar^2}{\gamma a^2 \sin(ka)}$ (d) $\frac{\hbar^2}{2\gamma a^2 \sin(ka)}$

Soln. **(A)** $\text{Energy density} = \frac{L}{\pi\left(\frac{dE}{dk}\right)} = \frac{L}{\pi\left[\frac{d}{dk}\{E_0 - \beta - 2\gamma\cos(ka)\}\right]} = \frac{L}{2\pi\,\gamma\, a \sin ka}$.

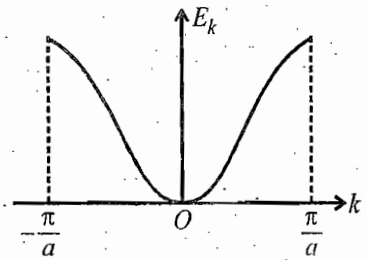
Hence, correct option is (b).

(B) $\text{Effective mass } (m^*) = \frac{\hbar^2}{\left(\frac{d^2E}{dk^2}\right)} = \frac{\hbar^2}{\frac{d}{dk}\left(\frac{d}{dk}\{E_0 - \beta - 2\gamma\cos(ka)\}\right)} = \frac{\hbar^2}{\frac{d}{dk}[2\gamma a \sin(ka)]}$

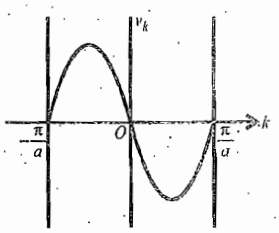
$$\Rightarrow \quad m^* = \frac{\hbar^2}{2\gamma a^2 \cos(ka)}$$

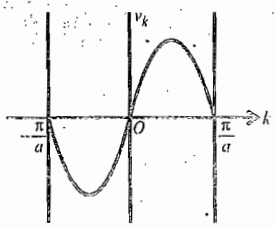
Hence, correct option is (b).

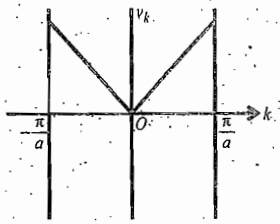
18. The energy, E_k for band electrons as a function as a function of the wave vector, k in the first Brillouin zone $\left(-\frac{\pi}{a} \le k \le \frac{\pi}{a}\right)$ of a one-dimensional monatomic lattice is shown as (a is lattice constant)

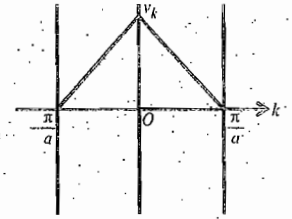


The variation of the group velocity v_k is most appropriately represented by [GATE 2014]

(a)


(b)


(c)


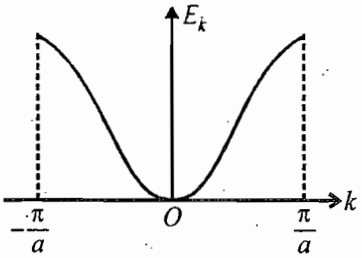
(d)


Soln. The velocity v can be given by

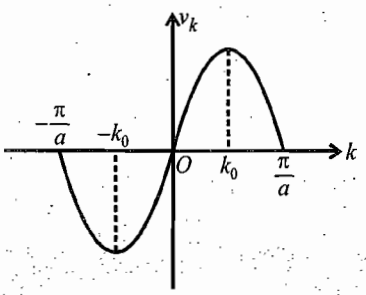
$$v = \frac{\hbar k}{m} = \frac{p}{m} \qquad \ldots (i)$$

This shows that, for a free electron, v is proportional to k. However, in the band theory, E_k is generally not proportional to k. The variation of E with k based on the band theory is shown in figure (below).

Here, $v = \frac{1}{k}\cdot\frac{dE}{dk}$ ... (ii)



This graph shows that the slope dE/dk of the $E(k)$ curve is not constant but changes with k. Using this curve and employing equation (ii), one can obtain v versus k as shown in figure (below).



This curve indicates that the velocity of the electron is zero for $k = 0$ and $\pm\frac{\pi}{a}$, where the slope dE/dk is zero. i.e. at the top and bottom of the energy band (first Brillouin zone). For $k = k_0$, where k_0 corresponds to the inflexion point of $E(k)$ curve, the absolute value of the velocity attains a maximum value equal to free electron velocity. Beyond this point, the velocity decreases with increase in energy.

Hence, correct option is (b).

19. The energy versus wave vector $(E-k)$ relationship near the bottom of a band for a solid can be approximated as $E = A(ka)^2 + B(ka)^4$, where the lattice constant $a = 2.1\,\text{Å}$. The values of A and B are 6.3×10^{-19} J and 3.2×10^{-20} J, respectively. At the bottom of the conduction band, the ratio of the effective mass of the electron to the mass of free electron is _____ (Give your answer upto two decimal places).

Take $\hbar = 1.05\times10^{-34}$ J-s, mass of free electron $= 9.1\times10^{-31}$ kg. **[GATE 2016]**

Soln. The ratio of effective mass to the free electron mass

$$= \frac{m_e^*}{m_e} = \frac{\frac{\hbar^2}{\left(\frac{d^2E}{dk^2}\right)}}{m_e} = \frac{\frac{\hbar^2}{\frac{d}{dk}\left\{2ka^2A + 4Bk^3a^4\right\}}}{m_e} = \frac{\frac{\hbar^2}{\left(2a^2A + 12Bk^2a^4\right)}}{m_e}$$

$$= \frac{\left(\frac{\hbar^2}{2a^2A}\right)}{m_e} \quad \{\text{at the bottom of conduction band } k = 0\}$$

$$= \frac{(1.05\times10^{-34})^2}{\frac{2\times(2.1\times10^{-10})^2\times(6.3\times10^{-19})}{(9.1\times10^{-31})}} = \frac{1.05\times1.05\times10^{-68}}{2\times2.1\times2.1\times10^{-20}\times6.3\times10^{-19}\times9.1\times10^{-31}} = \frac{1\times10^{2}}{8\times6.3\times9.1}$$

$$= \frac{10^2}{458.64} = 0.218 = 0.22$$

Hence, correct answer is (0.22).

20. Given the tight binding dispersion relation $E(k) = E_0 + A\sin^2\left(\frac{ka}{2}\right)$, where E_0 and A are constant and a is the lattice parameter. What is the group velocity of an electron at the second Brillouin zone boundary?

(a) 0 (b) $\frac{a}{h}$ (c) $\frac{2a}{h}$ (d) $\frac{a}{2h}$ **[JEST-2015]**

Soln. The dispersion relation is given by $E(k) = E_0 + A\sin^2\left(\frac{ka}{2}\right)$ ... (i)

Now, group velocity $V_g = \frac{d\omega}{dk} = \frac{\hbar}{\hbar}\frac{d\omega}{dk} = \frac{d(\hbar\omega)}{\hbar dk} = \frac{dE}{\hbar dk} = \frac{1}{\hbar}\cdot\frac{dE}{dk}$

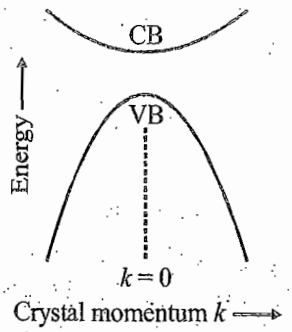
$$= \frac{1}{\hbar}\cdot\frac{d}{dk}\left(E_0 + A\sin^2\left[\frac{ka}{2}\right]\right) = \frac{1}{\hbar}\left(0 + A\cdot 2\sin\left(\frac{ka}{2}\right)\cdot\cos\left(\frac{ka}{2}\right)\cdot\frac{a}{2}\right) = \frac{1}{\hbar}\cdot A\sin\left(\frac{ka}{2}\right)\cos\left(\frac{ka}{2}\right).$$

At the boundary of second Brillouin zone i.e., at $k = \pm\frac{\pi}{2a}$,

$$V_g\Big|_{k=\pm\frac{2\pi}{a}} = \left.\frac{d\omega}{dk}\right|_{k=\pm\frac{2\pi}{a}} = \frac{1}{\hbar}\cdot A\sin\left(\pm\frac{2\pi}{a}\cdot\frac{a}{2}\right)\cdot\cos\left(\pm\frac{2\pi}{a}\cdot\frac{a}{2}\right) = \left(\frac{1}{\hbar}\right)\sin(\pm\pi)\cos(\pm\pi) = 0.$$

Hence, correct option is (a).

21. Suppose the energy band diagram of a certain pure crystalline solids as shown in the figure below, where the energy (E) varies with crystal momentum (k) as $E \propto k^2$.



At finite temperatures the bottom of the conduction band (CB) is partially filled with electrons (e) and the top of the valence band (VB) is partially filled with holes (h). If an electric field is applied to this solid, both e and h will start moving. If the time between collisions is the same for both e and h, then

(a) e and h will move with the same speed in opposite directions
(b) h will on an average achieve higher speed than e
(c) e will on an average achieve higher speed than h
(d) e and h will recombine and after a while there will be no flow of charges **[TIFR-2012]**

Soln. When an electric field will be applied, hole will achieve higher speed than electron.

Hence, correct option is (b)

PRACTICE SET

1. The effective mass of an electron in a semiconductor can be
   (a) negative near the bottom of the end
   (b) a scalar quantity with a small magnitude
   (c) zero at the center of the band
   (d) negative near the top of the band

2. Consider the energy E in the first Brillouin zone as a function of the magnitude of the wave vector k for a crystal of lattice constant a. Then,
   (a) the slope of E versus k is proportional to the group velocity.
   (b) the slope of E versus k has its maximum value at $|k| = \frac{\pi}{a}$.
   (c) the plot of E versus k will be parabolic in the inteval $\left(-\frac{\pi}{a}\right) < k < \left(\frac{\pi}{a}\right)$.
   (d) the slope of E versus k is non zero for all k in the interval $\left(-\frac{\pi}{a}\right) < k < \left(\frac{\pi}{a}\right)$.

3. The effective mass of an electron in a semiconductor
   (a) can never be positive
   (b) can never be negative
   (c) can be positive or negative
   (d) depends on its spin

4. Density of states of free electrons in a solid moving in a solid with an energy 0.1 eV is given by 2.15×10^{21} eV^{-1} cm^{-3}. The density of state (in eV^{-1} cm^{-3}) for electrons moving with an energy of 0.4 eV will be
   (a) 1.07×10^{21} (b) 1.52×10^{21} (c) 3.04×10^{21} (d) 4.3×10^{21}

5. The energy $E(\vec{k})$ of electrons of wave vectors $\vec{k}$ in a solid is given by $E(\vec{k}) = Ak^2 + Bk^4$, where A and B are constants. The effective mass of the electron at $(\vec{k}) = k_0$ is
   (a) Ak_0^2 (b) $\frac{\hbar^2}{2A}$ (c) $\frac{\hbar^2}{(2A + 12\,Bk_0^2)}$ (d) $\frac{\hbar^2}{Bk_0^2}$

6. The order of magnitude of the energy gap of a typical semiconductor is
   (a) 1 MeV (b) 1 keV (c) 1 eV (d) 1 meV

7. A beam of X-ray of intensity I_0 is incident normally on a metal sheet of thickness 2 mm. The intensity of the transmitted beam is $0.025\ I_0$. The linear absorption coefficient of the metal sheet (in per m) is_____. (upto one dimensional place).

8. The energy dependence of the intensity of states for a two dimensional non-relativistic electron gas is given by, $g(E) = CE^n$, where C is constant. The value of n is_____.

9. Given that the Fermi energy of gold is 5.54 eV, the number density of electrons is_____ $\times 10^{28}$/m^3 (upto one dimensional place).

10. In a crystalline solid, the energy band structure (E-k relation) for an electron of mass m is given by $E = \frac{\hbar^2 k\,(2k - 3)}{2m}$. The effective mass of the electron in the crystal is
    (a) m (b) $\frac{2}{3}m$ (c) $\frac{m}{2}$ (d) $2m$

11. Fermi energy of a certain metal M_1 is 5 eV. A second metal M_2 has an electron density which is 6% higher than that of M_1. Assuming that the free electron theory is valid for both the metals, the Fermi energy of M_2 is closest to
(a) 5.6 eV (b) 5.2 eV (c) 4.8 eV (d) 4.4 eV

12. In the Kronig-Penney model, electrons are assumed to be moving in
(a) one-dimensional square well potential (b) one-dimensional square well periodic potential
(c) three-dimensional coulomb potential (d) a periodic harmonic potential

13. Indicate the false conclusion drawn from the Kronig-Penney model, of band theory of solids
(a) The energy spectrum consists of a number of allowed energy bands separated by forbidden regions
(b) The width of allowed energy bands decreases with increasing energy
(c) The width of a particular energy band decreases with increasing binding energy of the solid
(d) The total number of possible wave functions in any energy band is equal to the number of unit cells

14. Lattice forces effect the motion of electrons in a metallic crystal, so that the relationship between the energy E and wave number k is not the classical equation $E = \frac{\hbar^2 k^2}{2m}$, where m is the electron mass. Instead, it is possible to use an effective mass m^* given by which of the following

(a) $m^* = \frac{1}{2}\hbar^2 k\left(\frac{dk}{dE}\right)$ (b) $m^* = \frac{\hbar^2 k}{\left(\frac{dk}{dE}\right)}$

(c) $m^* = \hbar^2 k\left(\frac{d^2k}{dE}\right)^{1/3}$ (d) $m^* = \frac{\hbar^2}{\left(\frac{d^2E}{dk^2}\right)}$

15. In the Kronig-Penney model, the discontinuities in E versus k curve occur for
(a) $k = \frac{n\pi}{a}$ (b) $k = \frac{8n\pi}{a}$ (c) $k = \frac{n^2\pi}{a}$ (d) $k = \frac{n\pi}{4a}$

16. Assume that the heat capacity at constant volume of a metal varies as $aT + bT^3$ at low temperatures. The temperature dependence of entropy is given by
(a) $aT + bT^3$ (b) $a + bT^2$ (c) $aT + \frac{bT^3}{3}$ (d) $aT^2 + bT^4$

ANSWER KEY

1. (d)	2. (c)	3. (c)	4. (d)	5. (c)	6. (c)	
7. (1.845×10^3 per meter)	8. (0)	9. (5.9)	10. (c)	11. (b)	12. (b)	
13. (b)	14. (d)	15. (a)	16. (c)			

Chapter 8

SEMICONDUCTORS

Energy bands in a solid:

In case of a solid the atoms are arranged in systematic space lattice and hence atom is greatly influenced by neighbouring atoms. Due to this closeness of atoms electrons will be intermixed with neighbouring atoms. Due to this intermixing number of permissible energy levels increases and there are significant changes in the energy levels. So in case of solid instead of single energy levels there will be bands of energy levels associated with single atom. A set of such closely packed energy levels is called an energy band.

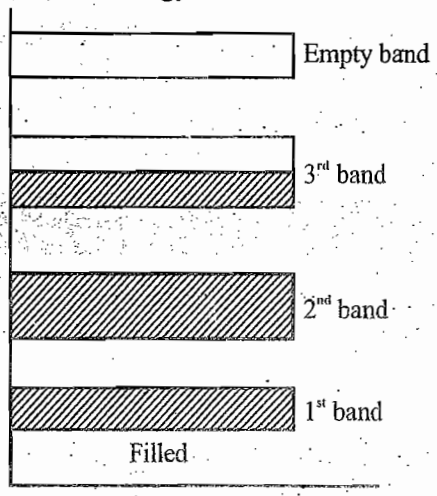
Concept of energy band formation:

Energy levels of a single isolated atom of silicon is shown in figure.

$$\mathrm{Si}(14) \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^2$$

Each silicon atom has 14 electrons of which 2 electrons occupy K-shell, 8 occupy L-shell and 4 occupy M-shell. Two electrons of M shell are in subshell $3s$ and two are in subshell $3p$ i.e. $3p$ subshell is half-filled because it can accommodate a total of 6 electrons.

For a large number of atoms in crystalline silicon, these shells differ in extremely small amounts of energy and are merged together to form one energy band.



Energy band in solid state

Valence band, conduction band and Forbidden band:

1. Valence band : The electrons in outermost shell are called valence electrons. The band formed by a series of energy levels containing valence electrons is known as valence band (VB). This is the highest energy occupied band. Valance band may be partially or completely filled and can never be empty.

2. Conduction band : In certain materials, valence electrons are loosely attached to the nucleus. These vale nce electrons leave the valence band and enter into a band known as conduction band (CB). This is defined as lowest unfilled energy band. The band may be empty or partially filled. If conduction band does not have electrons then current conduction will not be possible.

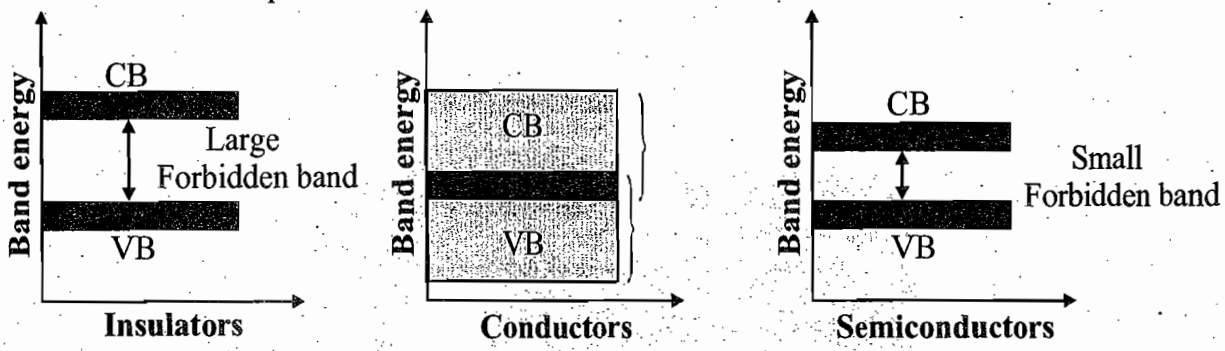
3. Forbidden band: Separation between conduction band and valence band is known as forbidden energy gap. There is no allowed energy state in this gap and hence no electron can stay in forbidden energy gap. Greater is the energy gap means more tightly the valence electrons are bound to nucleus.

Insulators, conductors and semiconductors :

1. Insulators : For insulators, forbidden energy band is wide and electrons from VB cannot jump into CB. It is of the order of 10 eV at $T = 0$ K and all electrons will be in VB. The resistivity of insulator is of the order of 10^7 Ω-meter.

2. Conductors: In this case, forbidden band is absent and VB and CB overlap each other. Due to overlapping of VB and CB, a slight potential difference across the conductor causes the free electrons to constitute electric current. Due to absence of forbidden band there is no structure to establish holes and total current is simply due to flow of electrons.

3. Semiconductor: Semiconductor material is one whose electrical conductivity lies between insulators and good conductors. Generally energy gap is of the order of 1 eV. At $T = 0$ K, there are no electrons in conduction band and VB is completely filled. When a small amount of energy is applied then electrons can move easily from VB to CB. If temperature is increased then forbidden band is decreased.

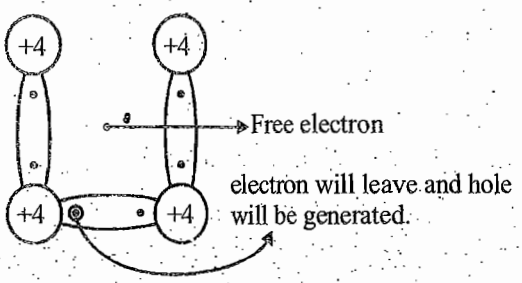


Conductivity of a semiconductor:

Materials like Ge and Si have resistivity of order of 10^{-4} to 0.5 Ω-meter. Conductivity of a semiconductor increases with increase in temperature, i.e. resistivity will decrease with increase in temperature. Therefore semiconductors have negative temperature coefficient of resistance.

Effect of temperature on semiconductor:

At $T = 0$ K, semiconductor crystal behaves as a perfect insulator because covalent bonds are very strong and no free electrons are available. At $T = 0$ K, VB is filled but no electron can reach CB to become free electron. At room temperature some of the covalent bonds are broken due to the thermal energy supplied to crystal, and due to the breaking of the bonds, some electrons become free which were engaged in formation of these bands.



Effect of temperature on forbidden energy gap (E_G):

For silicon : $E_G(T) = 1.21 - 3.6 \times 10^{-4}\, T$, where T is in 0 K.

At $T = 0$ K $\rightarrow E_G = 1.21$ eV

$T = 25$ °C $\rightarrow E_G = 1.1$ eV

For germanium : $E_G(T) = 0.785 - 2.2 \times 10^{-4}\, T$

At $T = 0$ K $\rightarrow E_G = 0.785$ eV

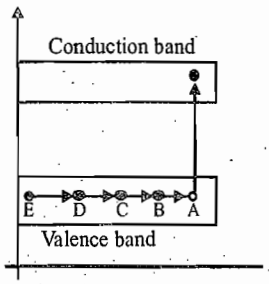
$T = 25$ °C $\rightarrow E_G = 0.72$ eV

So, at room temperature energy required to break the covalent bond is 0.72 eV for Ge and 1.1 eV for Si. So, at room temperature electrons move from VB to CB.

Concept of holes:

At room temperature when covalent bonds are broken then electrons leaves the vicinity of an atom and leaves a positive charge behind. This positive charge is called hole. So hole is the nothing but missing electron in the covalent bond.

Due to thermal energy an electron leaves the VB and enter into conduction band. This electron leaves a vacancy in valence band at A. Now valance electron B, comes at A to fill hole at A. This process is repeated and valence electron move along path EDCBA while hole move along the path ABCDE. Here hole current is due to the movement of valence electrons from one covalent band to another covalent band. The conductivity of Ge increases by about 6 % per degree increasing in temperature. While in Si it is about 8 % per degree increase in temperature.

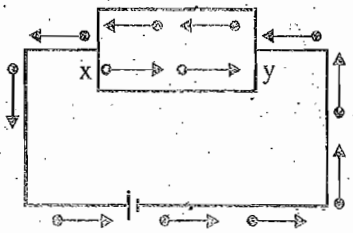


Types of semiconductors:

1. Intrinsic semiconductors:

It is an extremely pure form of semiconductor in which electrons and holes are created by thermal excitation. The electrons reaching the CB due to the thermal excitation leave equal number of valencies or holes in VB. In case of intrinsic semiconductor, number of free electrons is always equal to number of holes.

Current flow in intrinsic semiconductors:



When an external field is applied across an intrinsic semiconductor then conduction through semiconductor is by both electrons and holes.

Free electrons in CB move towards the positive terminal of battery while holes in VB move towards negative terminal of battery. Therefore, total current inside the semiconductor is sum of currents due to both electrons and holes. Current in external wire is due to electrons only, not due to holes. When holes reach at negative terminal *y* then electrons reaching here combine with holes and these holes are destroyed. Now again new holes are created and process is continued.

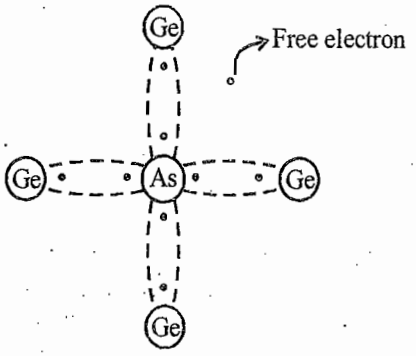
2. Extrinsic semiconductors:

The electrical conductivity of intrinsic semiconductors can be increased by adding some impurity in process of crystallization. The added impurity is very small of the order of one atom per million atoms of pure semiconductor. However the increase in conductivity by addition of minute impurities is about 20 times.

Types of extrinsic semiconductors:

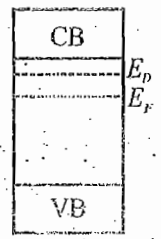
(A) N-type: When doping material is pentavalent atoms e.g. Bi, Sb, As and P.

This atom is known as donor atom because it donates one electron to CB of pure, semiconductor.
When a small amount of pentavalent impurity is added to a pure semiconductor cyrstal during crystal growth, the resulting crystal is known as N-type extrinsic semiconductor.



Arsenic atom fits in Ge crystal in such a way that its four valence electrons form covalent bonds with four Ge atoms. The fifth electron of As atom is not covalently bonded but it is loosely bound to parent Arsenic atom. The amount of energy needed to detach this 5th valance electron from impurity atom is of the order of only 0.01 eV for Ge and 0.05 eV for Si. This energy is very small and may be provided with thermal agitation at room temperature. Such a liberated valence electron is then free to move in a cuptal lattice in same way as free electrons in an intrinsic semiconductor. So, by addition of pentavalent atom the concentration of electrons in CB is increased. When pentavalent atom gives one electron then as at on becomes positively charged ion. This Arsenic atom cannot take part in conduction because it is firmly fixed into crystal lattice.

Fifth left over valence electron is not accommodated in VB, but moves to CB. Although each Arsenic atom provides only one free electron, yet an extremely large amount of Arsenic impurity provides enough atoms to supply millions of free electrons.



N-type semiconductor

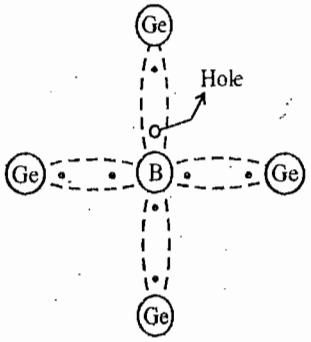
Important points about N-type semiconductor:

(i) Number of electrons is larger than number of holes.

(ii) It is electrically neutral, because extra electrons are created by addition of neutral pentavalent impurity atoms to semiconductor. Therefore, no extra positive or negative charge is added.

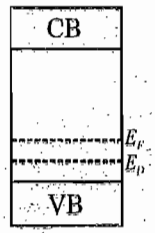
(iii) When N-type semiconductor is placed between two electrodes and an electric field is applied then excess electrons donated by impurity atoms will travel towards the positive electrode. This constitutes the electric current.

(B) P-type: When doping material is trivalent atoms such as Ga, In, Al and B (which have three valence electrons). This trivalent atom is known as acceptor atom because it accepts one electron from semiconductor atoms.



When boron is added to Ge then each atom of boron fits into Ge crystal with only three covalent bonds. Here 3 valence electrons of boron atom form covalent bonds with valence electrons of Ge atom. For fourth covalent bond one valance electron will care from Ge and there is deficiency of one electron which is called hole.

So for each boron atom added, one hole is created, a small amount of boron provides million of holes.



P-type semiconductor

Impurity atoms are called acceptor because they accept electrons from Ge atoms. Since current carriers are positively charged particles (holes). This type of semiconductor is a P-type semiconductor.

Important points about P-type semiconductors:

(i) Number of holes is larger than number of electrons.

(ii) P-type semiconductor remains electrically neutral as the number of mobile holes under all conditions remains equal to number of acceptors.

(iii) When an electric field is applied the current conduction is predominantly by holes. Holes are positively charged they are directed towards negative terminal and constitute the hole current. In P-type valance electrons move from one covalent bond to another covalent bond.

Charge neutrality in a semiconductor:

Let n and p are electrons and hole concentration respectively and n_i is intrinsic concentration. If N_D be the concentration of donor atoms. As donor atoms are ionized at room temperature then there will be N_D immobile positive charges per cubic meter contributed by donor ions. Therefore, total positive charge be $(N_D + p)$ if N_A be the concentration of acceptor atoms. In this case, there will be N_A immobile negative charges per cubic meter. Therefore, total negative charge will be $(N_A + n)$.

But semiconductor is neutral therefore, $n + N_A^- = N_D^+ + p$.

Law of mass action :

According to this law, "Under thermal equilibrium the product of concentration (n) of free electrons and concentration (p) of holes remains constant". It is independent of the amount of doping by donor and acceptor impurities.

Here $n.p = n_i^2$, where $n_i^2 = A_0 T^3 e^{-(E_g/k_B T)}$ is called law of mass action.

This law is valid for both intrinsic and extrinsic semiconductors.

Charge density in N and P-type semiconductor :

(A) N-Type:

$$n + N_A^- = N_D^+ + p$$

For N-type semiconductors, there is no acceptor doping.

Therefore, $N_A^- = 0$ and n >> p

Therefore, $n = N_D^+$

Therefore, in N-type semiconductors, free electron concentration is approximately equal to density of donor atoms.

$$n.p = n_i^2 \quad \Rightarrow \quad p = \frac{n_i^2}{N_D^+}$$

(B) P-Type:

$$n + N_A^- = N_D^+ + p$$

For P-type semiconductors, there is no donor doping therefore, $N_D^+ = 0$ and $p >> n$

Therefore, $p = N_A^-$

Therefore, in case of P-type semiconductors, hole concentration is approximately equal to density of acceptor atoms.

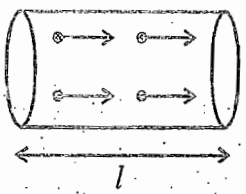
$$n.p = n_i^2 \quad \Rightarrow \quad n = \frac{n_i^2}{N_A^-}$$

Ohm's law for conduction current:

$J = \sigma E$ is ohm's law for conduction current.

Let n is number of electrons per cm^3 and N is total number of electrons per cm^3.

$$N = n.q$$



Let A is area of cross section and ℓ is length of conductor then total charge

$$Q = n \cdot q \cdot A \cdot \ell$$

Let electrons move with velocity v_d then total time to travel $T = \frac{\ell}{v_d}$

Therefore, total current = $I = \frac{Q}{T} = \frac{nqA\ell}{\ell}.v_d$

Current density $(J) = \frac{I}{A} = nqv_d = nq\mu E$

If $\sigma = nq\mu \quad \Rightarrow \quad J = \sigma E$

Conductivity of N-type is $\sigma_n = nq\mu_n$

Conductivity of P-type is $\sigma_p = pq\mu_p$.

Conductivity:

Conductivity of a metal is different from conductivity of a semiconductor. In case of N-type semiconductor conduction is by electrons while in P-type semiconductor conduction is by holes. For intrinsic semiconductor conductivity depends upon both electrons and holes.

1. Conductivity of intrinsic semiconductor:

$$\sigma_i = nq\mu_n + pq\mu_p$$

For intrinsic semiconductors, $n = p \quad \Rightarrow \quad n = p = n_i$

Therefore, $\sigma_i = n_i q(\mu_n + \mu_p)$

Resistivity of intrinsic semiconductors is $\rho_i = \frac{1}{n_i q(\mu_n + \mu_p)}$

2. Conductivity of N-type semiconductor:

$$\sigma_n = nq\mu_n$$

For N-type, $n = N_D^+$

$$\sigma_n = N_D^+ \cdot q \cdot \mu_n \ (n >> p)$$

3. Conductivity of P-type semiconductors:

$$\sigma_p = pq\mu_p$$

For P-type, $p = N_a^-$

$$\sigma_p = N_a^- \cdot q \cdot \mu_p \ (p >> n).$$

Variation of mobility w.r.t. electric field:

1. If $E < 10^3$ v/cm then $\mu \rightarrow$ constant

2. If 10^3 v/cm $< E < 10^4$ v/cm then $\mu \propto E^{-1/2}$

3. If $E > 10^4$ v/cm then $\mu \propto E^{-1}$.

For low value of electric field mobility is constant but for higher value of electric field mobility is inversely proportional to electric field.

Fermi- Level:

The Fermi-Dirac distribution:

The equation for $f(E)$ is called the Fermi-Dirac probability function and specifies the fraction of all states at energy E(electron volt) occupied under conditions of thermal equilibrium $f(E)$ is defined as

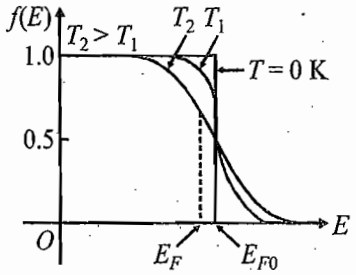
$f(E) = \frac{1}{1+e^{(E-E_F)/k_BT}}$, where k_B is Boltzmann constant in eV/K and T is temperature in K.

E_F is Fermi level or characteristic energy for crystal in eV.

Definition of E_F:

The Fermi-level represents the energy state with 50 % probability of being filled if no forbidden band exists. If $E = E_F$ then $f(E) = 1/2$, for any value of temperature.

Plot of $f(E)$ versus E :



When $T = 0$ K:

Case 1: If $E > E_F$ then exponential term becomes infinite and $f(E) = 0$. Consequently there is no probabilities of finding an occupied quantum state of energy greater than E_F at absolute zero.

Case 2: If $E < E_F$ then exponential term becomes zero and $f(E) = 1$. All quantum levels with energies less than E_F will be occupied at $T = 0$ K.

Energy density:

$$dn_e = \rho_E dE \qquad \ldots (1)$$

where dn_e is number of free electrons per cubic meter whose energies lie in internal dE.

$\rho_E \rightarrow$ Density of electrons, i.e. number of electron per electron volt per cubic meter of metal.

But $\rho_E = f(E)N(E)$ ... (2)

$N(E) \rightarrow$ Density of states i.e number of states per electron volt per cubic meter in conduction band

$f(E) \rightarrow$ Probability that a quantum state with energy E is occupied by an electron.

The expression $N(E)$ is given by $N(E) = \gamma E^{1/2}$ ... (3)

Where γ is a constant.

$$\gamma = \frac{4\pi}{h^3}(2m)^{3/2}\left(1.6\times10^{-19}\right)^{3/2} = 6.82\times10^{27}\left(m^{-3}\right)(eV)^{-3/2}$$

Energy distribution in a metal:

$\rho_E = \gamma E^{1/2}$ For $E < E_F$

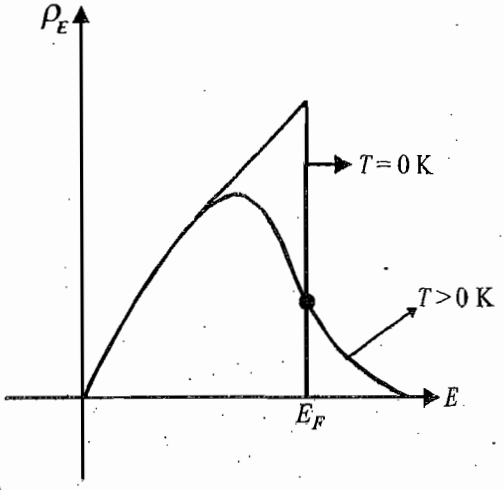
$= 0$ For $E > E_F$

this relationship is known as completely degenerate energy distribution function.

Fermi energy is the maximum that any electron may posses at absolute zero. Fact that the electrons actually have energies extending from 0 to E_F at absolute zero is a consequence of Pauli exclusion principle which state that no two electron may have the same set of quantum numbers. Hence not all electrons can have the same energy even at 0 K.

Plot of ρ_E versus E:

The distribution function changes only very slightly with temperature even though the temperature is as great at 2500 K. The effect of high temperature is merely to give those electrons having the high energies at absolute zero.



Calculation of Fermi level:

The area under the curve of given figure represents the total number of free electrons. Thus

$$n = \int_0^{E_F} \gamma E^{1/2} dE = \frac{2}{3}\gamma E_F^{3/2} \quad \Rightarrow \quad E_F = \left(\frac{3n}{2\gamma}\right)^{2/3}$$

By putting the value of γ in above expression value of E_F will be $E_F = 3.64 \times 10^{-19}\, n^{2/3}$, where value of n varies from metal to metal and value of E_F is in eV.

For more practical cases value of E_F is less than 10 eV.

Calculation of number of electrons in conduction band:

$dn = \rho_E dE$

But $\rho_E = f(E)N(E)$

Therefore, $dn = f(E)N(E)dE$

where dn represents the number of conduction electrons per-cubic meter whose energy lies between E and $E+dE$ the density of states $n(E)$ is derived on the assumption that bottom of conduction band is at zero potential.

In a semiconductor, the lowest energy in conduction band is at E_C and so value of $N(E)$ must be:

$N(E) = \gamma(E - E_C)^{1/2}$ for $E > E_C$

The value of number of electrons in conduction band is given by

$$n = \int_{E_C}^{\infty} N(E) f(E) dE$$

For $E \geq E_C$, $E - E_F >> k_B T$; $f(E) = e^{-(E - E_C)/k_B T}$

$$n = \int_{E_C}^{\infty} \gamma (E - E_C)^{1/2} e^{-(E-E_C)/k_B T} dE = N_C e^{-(E-E_C)/k_B T}, \text{ where } N_C = 2\left(\frac{2\pi m_n k_B T}{h^2}\right)^{3/2}$$

Calculation of number of holes in valance band:

$N(E) = \gamma(E_V - E)^{1/2}$ for $E < E_V$

Value of number of electrons in conduction band is given by

$$p = \int_{-\infty}^{E_V} N(E) f(E) dE$$

For $E \le E_V$, $(E_F - E) >> k_B T$, $f(E) = e^{-(E_F - E)/k_B T}$

$$p = \int_{-\infty}^{E_V} \gamma (E_V - E)^{1/2} e^{-(E_F - E)/k_B T} dE = N_V \, e^{-(E_F - E)/k_B T}, \text{ Where } N_V = 2\left(\frac{2\pi m_p k_B T}{h^2}\right)^{3/2}$$

Position of Fermi level in an intrinsic semiconductor:

$n = N_C e^{-(E_C - E_F)/k_B T}$ and $p = N_V e^{-(E_F - E_V)/k_B T}$

For an intrinsic semiconductor, $n = p$

i.e. $N_C e^{-(E_C - E_F)/k_B T} = N_V e^{-(E_F - E_V)/k_B T} \quad \Rightarrow \quad E_F = \frac{E_C + E_V}{2} + \frac{3}{4} k_B T \ln\left(\frac{m_p}{m_n}\right)$

For an intrinsic semiconductor if effective mass of both electrons and holes are equal.

Then, $N_C = N_V$, then $E_F = \left(\frac{E_C + E_V}{2}\right)$. Hence, Fermi level lies in centre of forbidden energy band.

If $m_p > m_n$, then $E_F > \left(\frac{E_C + E_V}{2}\right)$.

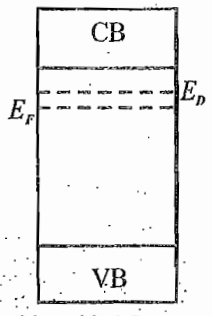
and if $m_p < m_n$ then $E_F < \left(\frac{E_C + E_V}{2}\right)$.

Position of Fermi level in N-type semiconductor:

$n = N_C e^{(E_C - E_F)/k_B T}$

For N-type semiconductors, $n = N_d^+ \quad \Rightarrow \quad E_F = E_C - k_B T \ln\left(\frac{N_C}{N_D^+}\right)$

Position of Fermi level in N-type semiconductors at room temperature:



Position of Fermi level in N-type semiconductors

At $T = 0$ K Fermi level is at CB but at room temperature Fermi level will be closer to CB but below donor level.

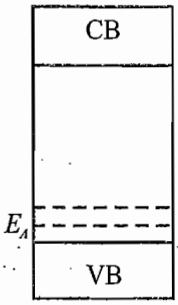
Position of Fermi level in P-type:

$$p = N_V e^{(E_F - E_V)/k_B T}$$

For P-type semiconductores, $p = N_A^-$

Therefore, $N_A^- = N_V e^{\frac{(E_F - E_V)}{k_B T}} \Rightarrow E_F = E_V + k_B T \ln\left(\frac{N_V}{N_A^-}\right)$.

At $T = 0$ K, $E_F = E_V$ but at room temperature Fermi level will be closer to VB but above acceptor level.



Position of Fermi level in P-type semiconductors

Effect of temperature in N-type and P-type semiconductors:

In case of N and P-type by increasing temperature number of electron hole pairs are increased. Ratio of number of electrons to number of hole (in case of N-type) and number of holes to number of electrons (in case of P-type) are decreased. Therefore, an extrinsic semiconductor behaves like an intrinsic semiconductor and Fermi level shifts towards centre of semiconductor.

Effect of doping on N-type and P-type semiconductors:

In case of N and P-type semiconductors by increasing doping (degenerate semiconductor) Fermi level shifts inside the CB in case of N-type and shifts inside the VB in case of P-type. Therefore, by increasing doping Fermi level shifts inside the bands.

Value of intrinsic concentration (n_i):

$n = N_C e^{-(E_C - E_F)/kT}$ and $p = N_V e^{-(E_F - E_V)/k_B T}$

Here, $p = N_V e^{-(E_F - E_V)/k_B T} \Rightarrow n_i^2 = N_C N_V e^{-(E_G/k_B T)}$

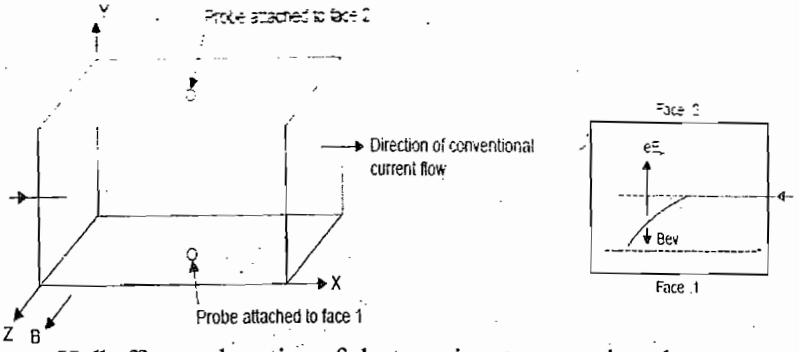
Where, $N_C = 4.82 \times 10^{21} \left(\frac{m_n}{m_0}\right)^{3/2} T^{3/2}$ and $N_V = 4.82 \times 10^{21} \left(\frac{m_p}{m_0}\right)^{3/2} T^{3/2}$

Therefore, $n_i^2 = \left(2.33 \times 10^{43}\right) \left(\frac{m_n m_p}{m_0^2}\right)^{3/2} T^{3/2} e^{-(E_G/k_B T)} \Rightarrow n_i^2 = A_0 T^3 e^{(E_G/k_B T)}$

Hall effect:

When a semiconductor is placed in a magnetic field $\vec{B}$ (along the z-direction) and a current density $\vec{J}$ (along x-direction) passed through it, a transverse electric field $\vec{E}$ (along y-direction) is set up given by $\vec{E} = R_H \vec{B} \vec{J}$ where R_H is the Hall coefficient or Hall constant.

The Hall effect may be explained with the help of following figure.



Hall effect and motion of electrons in *n*-type semiconductor

Assuming that the material is an *n*-type semiconductor, the current flow consists almost entirely of electrons moving from right to left just opposite to the conventional flow of current . If *v* is the velocity of electrons at right angles to the magnetic field, there is downward force on each electron of magnitude *Bev*. This causes the electron to be deflected in a downward direction and causes a negative charge to accumulate on the bottom face of the slab. A potential difference is therefore established from top to bottom of the specimen with bottom face negative. This potential difference causes a field E_H in the negative of *y*-direction, and so there is a force of eE_H acting in the upward direction on the electron. Equilibrium occurs when

$eE_H = eBv,\ E_H = Bv$

If J_x is the current density in the *x*-direction, then $J_x = nev$ where *n* is the concentration of current carriers.

Thus, $E_H = \frac{BJ_x}{ne};\ \frac{E_H}{BJ_x} = \frac{1}{ne}$

The Hall effect is described by means of the Hall coefficient R_H, defined in terms of the current density J_x by the relation $E_H = R_H J_x B \Rightarrow R_H = \frac{E_H}{J_x B} \Rightarrow R_H = \frac{1}{ne}$.

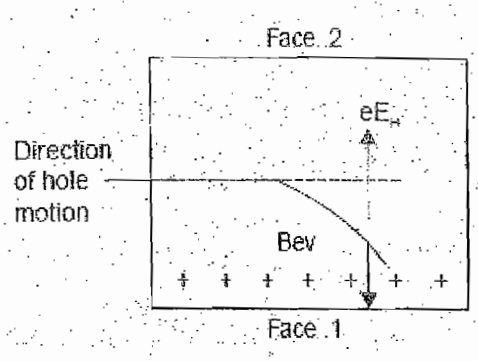
In this case $R_H = \frac{1}{ne}$.

Negative sign is used because the electronic field developed is in the negative *y*-direction.

i.e., $R_H = \frac{E_H}{J_x B} = -\frac{1}{ne}$.

All the quantities E_H, B and J_x can be measured, and so the Hall coefficient and carrier density *n* can be found out.

Figure shows the conditions that exist in a *p*-type semiconductor under identical conditions as that of *n*-type specimen described above.



Hall effect in *p*-type semiconductor

Experimental procedure :

The Hall coefficient is determined by measuring the Hall voltage that generates the Hall field. If V_H is the Hall

voltage across the sample of thickness t, then $V_H = E_H t$.

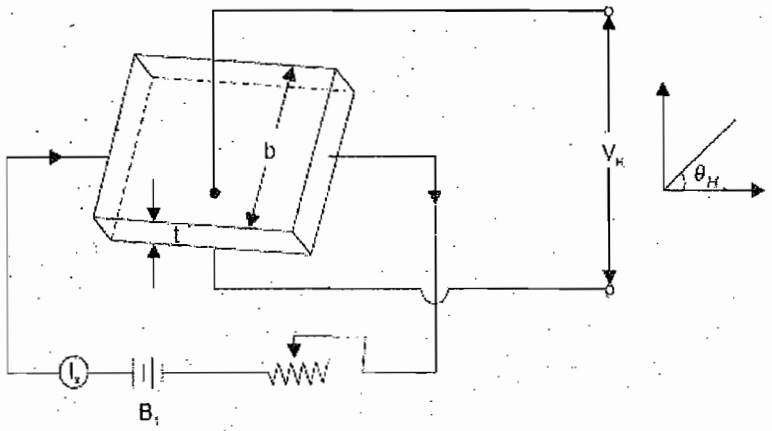
Substituting for E_H for equation $V_H = B\,t\,R_H\,J_x$.

If b is the width of the sample, then its cross-section will be $(b \times t)$ and the current density, $J_x = \frac{I_x}{bt}$.

$$V_H = \frac{B\,t\,R_H\,I_x}{bt} \text{ and } R_H = \frac{V_H b}{I_x B}$$

Note the polarity of V_H will be opposite for n and p-type.

A rectangular slab of the given material having a thickness t and width b is taken and a current I_x ampere is allowed to pass through this sample by connecting it to a battery. The slab is then placed between two pole pieces of an electromagnet such that if the current direction coincides with the x-axis, the magnetic flux density B coincides with the z-axis, as shown in the following figure.



Set up for the measurement of Hall voltage

The Hall voltage V_H is then measured by placing two probes at the centres of the bottom and top faces of the sample. If the magnetic flux density is B weber/m^2 and the Hall voltage is V_H volt, then R_H is obtained from above equations in m^3/coulomb. The analysis is given above applies only when the charge carriers are free of attractive forces in the energy bands and when they move with a steady drift velocity v_d. This is not the case in a semiconductor, and a computation of the average speed leads to the conclusion that

$$R_H = -\frac{3\pi}{8ne} = -\frac{1.18}{ne} \text{ instead of } -\frac{1}{ne}.$$

For n-type of material, the conductivity is given by $\sigma_n = ne\,\mu_n$ and $\mu_n = \frac{\sigma_n}{ne} = -\frac{\sigma_n R_H}{1.18}$.

For p-type material, $\mu_p = \frac{\sigma_p}{pe} = \frac{\sigma_p R_H}{1.18}$.

There is another interesting quantity called the Hall angle (θ_H) defined by the equation, $\tan\theta_H = \frac{E_H}{E_x}$

But $E_H = \frac{J_x B}{ne} = \frac{nev_x B}{ne} = \frac{v_x B E_x}{E_x}$.

Hence, $\tan\theta_H = \frac{E_H}{E_x} = \frac{v_x B}{E_x} = \mu B$, where μ is the mobility of the charge carriers.

Applications of Hall effect:

(i) Determination of type of semiconductor: For an *n*-type semiconductor the Hall coefficient is negative where as for a *p*-type semiconductor it is positive. Thus, the sign of the Hall coefficient can be used to determine whether a given semiconductor is *n*-type or *p*-type.

(ii) Calculation of carrier concentration (n).

(iii) Determination of mobility (μ).

(iv) Measurement of magnetic flux density (B).

SOLVED PROBLEMS

1. In a given N-type Si material if donor concentration is one atom per 2×10^8 silicon atoms. Assuming that effective mass of electron is equal to its true mass. Find the value of temperature at which Fermi-level coincides with the edge of conduction band density of atoms in Si is 5×10^{28} atoms per m^3.

Soln. $N_D = \dfrac{5\times10^{28}}{2\times10^8} = 2.5\times10^{20}/\text{m}^3$

It is given that $E_F = E_C$

Therefore, $N_D = N_C$

$$N_C = 4.82\times10^{21}\left(\frac{m_n}{m_p}\right)^{3/2} T^{3/2}$$

$$N_D = 2.5\times10^{20} = 4.82\times10^{21}\times T^{3/2} \quad (\because\ m_n = m_p)$$

Hence, $T = 0.14\ \text{K}$.

2. A Si semiconductor sample at T = 300 K is doped with phosphorus atoms at concentration of 10^{15} cm^3. What is the position of Fermi level with respect to intrinsic Fermi level.

Soln. $E_F - E_{Fi} = k_B T \ln\left(\dfrac{N_D}{n_i}\right)$

$$= 0.026\times\ln\left(\frac{10^{15}}{1.5\times10^{10}}\right) = 0.287\ \text{eV}$$

3. A hypothetical semiconductor has an intrinsic carrier concentration of $1.0\times10^{10}/cm^3$ at 300 K, it has conduction and valence band effective densities of states N_C and N_V both equal to $10^{19}/cm^3$.

(a) What is band gap.

(b) If the semiconductor is doped with $N_D = 1\times10^{16}$ donar/cm^3. What are the equilibrium electron and hole concentration at 300 K.

(c) If the piece of semiconductor, already having $N_D = 10$ donor/cm^3 is also doped with $N_A = 2\times10^{16}$ acceptor/cm^3. What are the new equilibrium electron hole concentration.

(d) Consistent with your answer to the part (c). What is the fermi level position with respect to the intrinsic fermi level ($E_F - E_{Fi}$).

Soln. (a) $n_i = (N_V N_C)^{1/2} e^{-E_g/2k_BT} \Rightarrow 10^{10} = 10^{19}\, e^{-E_g/2\times0.026\,\text{eV}}$

$\Rightarrow\ 10^{-9} = e^{-E_g/0.052\,\text{eV}} \Rightarrow \log(10^{-9}) = \dfrac{-E_g}{0.052\ \text{eV}}$

$\Rightarrow\ 20.72 = E_g/20.052 \Rightarrow E_g = 1.078\ \text{eV}$.

(b) $n_0 p_0 = n_i p_i$ (law of mass action)

$n_0 = N_D = 10^{16}$ (At room temperature)

$$p_0 = \frac{n_i^2}{n_0} = \frac{10^{20} \times 2.25}{10^{16}} \Rightarrow p_0 = 2.25 \times 10^4 / \text{cm}^3$$

(c) $N_D = 10^{16}$ donor/cm^3, $N_A = 2 \times 10^{16}$ acc./cm^3, $N_D^+ + p = N_A^- + n$

$\Rightarrow$ $10^{16} + p = 2 \times 10^{16} + n$ $\because$ p_0 dominant, therefore, n is neglected.

$\Rightarrow$ $10^{16} + p_0 = 2 \times 10^{16}$ $\Rightarrow$ $p_0 = 10^{16}/\text{cm}^3$

and $n_0 = \dfrac{10^{20}}{10^{16}} = 10^4/\text{cm}^3$, it becomes P-type

(d) $p_0 = n_i e^{\frac{E_i - E_F}{k_B T}}$ ($\because$ consistent with part (c))

$$\Rightarrow \quad \frac{10^{16}}{10^{10}} = e^{\left(\frac{E_i - E_F}{k_B T}\right)} \qquad \Rightarrow 10^6 = e^{\left(\frac{E_i - E_f}{k_B T}\right)}$$

$$\Rightarrow \quad 6 \times 2.303 \times 0.026 = E_i - E_f \qquad \Rightarrow E_i - E_f = 0.36 \text{ eV}$$

4. Show that

(a) Minimum conductivity of a semiconductor sample occurs when equilibrium constant electron.

$$n_0 = n_i \sqrt{\frac{\mu_p}{\mu_n}}$$

(b) What is expression for minimum conductivity.

(c) Compare $\sigma_{\min}$ with $\sigma_{\text{instrinsic}}$.

Soln. Let $\sigma = e\left(n\mu_n + p\mu_p\right)$

$$\sigma = e\left(n\mu_n + \frac{n_i^2}{n_0^2}\mu_p\right) \qquad \therefore \quad \frac{d\sigma}{dn} = 0$$

$$\mu_n - \frac{n_i^2}{n_0^2}\mu_p = 0 \Rightarrow \mu_n = \frac{n_i^2}{n_0^2}\mu_p \Rightarrow n_0^2 = n_i^2 \frac{\mu_p}{\mu_n}$$

For minimum conductivity $n_0 = n_i\sqrt{\dfrac{\mu_p}{\mu_n}}$; $p_0 = n_i\sqrt{\dfrac{\mu_n}{\mu_p}}$ Equilibrium concentration $\Rightarrow$ minimum conductivity.

(b) $\sigma_{\min} = e\left(n_0\mu_n + p_0\mu_p\right) = e\left(n_i\sqrt{\dfrac{\mu_p}{\mu_n}}\mu_n + n_i\sqrt{\dfrac{\mu_n}{\mu_p}}\mu_p\right) \Rightarrow \sigma_{\min} = n_i e\left(2\sqrt{\mu_p\mu_n}\right)$

(c) $\sigma_{\text{int}} = en_i\left(\mu_n + \mu_p\right) \Rightarrow \sigma_{\min} = n_i e 2\sqrt{\mu_p\mu_n} \Rightarrow \dfrac{\sigma_{\text{int}}}{\sigma_{\min}} = \dfrac{\mu_n + \mu_p}{2\sqrt{\mu_p\mu_n}}$

$$\sigma_{\text{int}} = \frac{\mu_n + \mu_p}{2\sqrt{\mu_p\mu_n}}\sigma_{\min}$$

5. A 0.46 μm thick sample of GaAs is illuminated with monochromatic light of $h\nu = 2$ eV, absorption coefficient $\alpha = 5\times10^4$ cm^{-1}. The power incident on the sample is 10 mW. Band gap of material is $E_g = 1.43$ eV find the total energy absorbed by the sample per second.

Soln. $x = 0.46 = 4.6\times10^{-5}$ cm^{-1}, $h\nu = 2$ eV, $\alpha = 5\times10^4$ cm^{-1}, $E_g = 1.43$ eV

$I_0 = 10$ mW. $\therefore$ $h\nu > E_g$

$\therefore$ $I_t = I_0 e^{-\alpha x}$

$= 10\, e^{-5\times10^4\times4.6\times10^{-5}} = 10\, e^{-23.0\times10^{-1}} = 10\times e^{-2.3}$

Transmit $\simeq 10\times e^{-2.3} = 1.002$

$\therefore$ Absorbed $= I_0 - 10\, e^{-2.3} = 10 - 1.002 = 8.998$ mW

6. A Si solar cell has a short circuited current of 100 mA and open circuit voltage of 0.84 V under full solar illumination. The fill factor is 0.7. What is the max power delivered to a load by this cell.

Soln. $I_{SC} = 100$ mA

$V_{OC} = 0.8$ V

$P_{max} = ?$ $\because$ $P_{max} = I_m V_m$ (to load)

$\frac{I_m V_m}{I_{SC} V_{OC}} = 0.7$ $\Rightarrow$ $\frac{I_m V_m}{100\times0.8} = 0.7$

$I_m V_m = 0.7\times100\times0.8 = 56$ mw

7. A photoconductive cell, $1\times1\times1$ mm^3 CdS crystal is illuminated with light of wavelength 450 nm and intensity 1 mw/cm^2. Assuming quantum efficiency of unity. Calculate the number of electron hole pairs generated per second given the energy band gap of CdS is 2.6 eV.

Soln. Given: $E_g = 2.6$ eV

$\because$ $I_{op} = g_{op} A_e (L_n + L_p + w)$

$A = 1\text{ mm}^2 = 10^{-2}$ cm^2

$t = 1$ mm $= 0.1$ cm

Q.E. $= 1$

$P_{in} = ?$ $I_{in}\times A = 10^{-3}$ W/cm^2 $\times 10^{-2}$ cm^2

$P_{in} = 10^{-5}$ W.

Sensitivity

$R = \frac{I_{op}}{P_{in}}$, Q.E. $= \frac{R\times0.1240}{\lambda(\text{nm})} = \frac{I_{op}\times1240}{P_{in}\times\lambda(\text{nm})} = 1 \Rightarrow \frac{I_{op}\times1240}{10^{-5}\times450} = 1$

$\Rightarrow$ $I_{op} = \frac{10^{-5}\times450}{1240} = 3.63\times10^{-6}$ A $= 3.63$ μA $\because$ $I_{op} = eA\, g_{op} t$

$\Rightarrow$ $3.63\times10^{-6} = 1.6\times10^{-19}\times10^{-2}\times g_{op}\times0.1$

$\Rightarrow$ $g_{op} = \frac{3.63\times10^{-6}}{1.6\times10^{-19}\times10^{-2}\times0.1}$

$\Rightarrow$ $g_{op} = 2.27\times10^{16}/\text{cm}^3 - \text{sec}$

8. Given that the density of states related effective masses of electrons and holes in Si are approximately 1.08 m_e and 0.56 m_e respectively, and the electron and hole drift. mobility at room temperature are 1350 and 450 $cm^2V^{-1}s^{-1}$ respectively. Calculate the intrinsic concentration and intrinsic resistivity of Si.

Soln. Since $N_C = 2\left(\frac{2\pi m_n * k_B T}{h^2}\right)^{3/2}$ and $N_V = 2\left(\frac{2\pi m_p * k_B T}{h^2}\right)^{3/2}$

Given, $N_C = 2.8 \times 10^{19}\ cm^{-3}$ and $N_V = 1.05 \times 10^{19}\ cm^{-3}$

Intrinsic concentration $n_i = \left(N_C N_V\right)^{1/2} \exp\left(\frac{-E_g}{2k_B T}\right) = 1 \times 10^{10}\ cm^{-3}$

Conductivity $\sigma = en_i\mu_n + en_i\mu_p = en_i\left(\mu_n + \mu_p\right) = 2.9 \times 10^{-6}\ \Omega^{-1}cm^{-1}$

and $\rho = \frac{1}{\sigma} = 3.5 \times 10^5\ \Omega\ cm$.

9. Estimate the mean speed of electrons in the conduction band of Si.

Soln. Average K.E. $= \frac{1}{2}m_e v_e^{\,2} = \frac{3}{2}k_B T$

$\Rightarrow \quad v_e = \left(\frac{3k_B T}{m_e}\right)^{1/2} = 2.3 \times 10^5\ ms^{-1}$.

10. The intrinsic resistivity of Germanium at 300 K is 0.47 Ω-m. The electron mobility (μ_n) at 300 K in Germanium is 0.39 m^2/Vs. The hole mobility $\mu_p = 0.19\ m^2/Vs$. Calculate density of electrons in the intrinsic material. Also calculate the drift velocity of holes and electrons for an electric field $E = 10^4$ V/m.

Soln. We have $\rho_i = 0.47\ \Omega$-m $\quad \Rightarrow \sigma_i = \frac{1}{\rho_i} = \frac{1}{0.47} = 2.12766.$

Density of electrons $= n_i = \frac{\sigma_i}{e(\mu_n + \mu_p)} = 2.293 \times 10^{19}/m^3$

Drift velocity of electrons $v_n = \mu_n E = 3900$ m/ sec.

Drift velocity of holes $v_p = \mu_p E = 1900$ m/sec.

11. Find the conductivity of Intrinsic Ge at 300 K. If donor type impurity is added to the extent of 1 impurity atom in 10^7 Ge atom, find the conductivity.

Given $n_i(300\ K) = 2.5 \times 10^{13}/cm^3$, $\mu_n = 3800\ cm^2/Vs$, $\mu_n = 1800\ cm^2/Vs$.

Soln. $\sigma_i = n_i e\left(\mu_n + \mu_p\right) = 0.0224$ siemen per meter

Number of Ge atoms/$cm^3 = 4.41 \times 10^{22}$.

Donor Impurity = 1 donor atom /10^7 Ge atom.

Concentration of donor atom $N_D = 4.41 \times 10^{22}$

Concentration of electron $n = N_D = 4.41 \times 10^{15}$

Concentration of holes $p = \frac{n_i^2}{N_D} = \frac{(2.5\times10^{13})^2}{4.41\times10^{15}} = 1.417\times10^{11}$ holes/c

Therefore, conductivity of N-type Ge semiconductor $\sigma_n = eN_D\mu_n = 2.68$

12. A potential difference of 10 V is applied longitudinally to a rectangular specimen of intrinsic Ge of length 25 mm, width 4 mm and thickness 1.5 mm. Determine at room temp.
(i) electron and hole drift velocities.
(ii) conductivity of intrinsic Ge. If intrinsic carrier density is 2.5×10^{19} /m^2
(iii) total current.

Soln. Applied voltage $V = 10$ V

Length of specimen $E = \frac{V}{l} = \frac{10}{0.025} = 400$ V/m

Electron drift velocity $v_n = \mu_n \times E = 0.38\times400 = 152$ m/sec

Hole drift velocity $v_p = \mu_p \times E = 0.18\times400 = 72$ m/sec

Intrinsic carrier concentration
$n_i = 2.5 \times 10^{19}$ /m^2

(ii) Intrinsic conduction $= \sigma_i = n_i e(\mu_n + \mu_p) = 2.24$ si/m

(iii) Total current I $= \sigma_i Ea = 2.24 \times 400 \times 4 \times 10^{-3} \times 1.5 \times 10^{-3} = 5.376$ mA.

13. Find the problem of occupancy of a staff of energy
(a) 6.05 eV above fermi energy
(b) 0.05 eV below fermi energy

Soln. At $T = 300$ K, $E_F = k_B T_F = 1.38 \times 10^{-23} \times 300$ J $= 414 \times 10^{-23}$ J $= 0.025$ eV.

$$f(E) = \frac{1}{\left(e^{(E-E_F)/k_BT}+1\right)} = \frac{1}{\left(e^{(0.05-0.025)/0.025}+1\right)} = 0.119 \text{ or } 12\%$$

$$f(E) = \frac{1}{\left(e^{(-0.05-0.025)/0.025}+1\right)} = \frac{1}{1.367} = 0.7315 \text{ or } 73.15\%.$$

14. A sample of silicon of thickness 200 μm is doped with 10^{23} phosphorus atoms per m^3. If the sample is kept in a magnetic field of 0.2 Wb/m^2 and a current of 1 mA is passed through the same, the Hall voltage produced is
(a) 62.5 μV (b) −6.25 μV (c) +6.25 μV (d) −62.5 μV **[GATE 2001]**

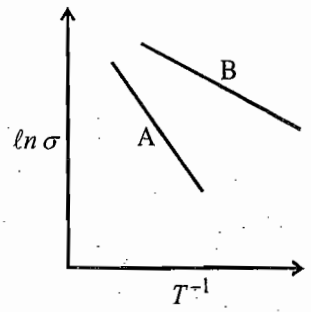
Soln. Hall voltage is defined as :

$$V_H = \frac{BI}{tne} = \frac{0.2\times1\times10^{-3}}{200\times10^{-6}\times10^{23}\times1.6\times10^{-19}}$$

$$= \frac{0.2\times10^{-1}}{200\times1.6} = 0.625\times10^{-4} = 62.5\ \mu\text{V}.$$

Here, in this question, the silicon is doped with phosphorus (P) which is pentavalent. Therefore, the Hall voltage will be produced by electrons and will be of negative type.
Hence, correct option is (d).

15. The temperature dependence of the electrical conductivity σ of two intrinsic semiconductors A and B is shown in the figure. If E_A and E_B are the bands gaps of A and B respectively, which one of the following is true ?



(a) $E_A > E_B$ (b) $E_A < E_B$ **[GATE 2004]**

(c) $E_A = E_B$ (d) E_A and E_B both depend on temperature

Soln. $\because$ Slope of the $\ell n\,\sigma$ versus T^{-1} graph is $-\frac{E}{2k_B}$, also from the given figure, slope of A < slope of B.

$$\Rightarrow \quad -\frac{(E)_A}{2k_B} < -\frac{(E)_B}{2k_B} \quad \Rightarrow \quad E_A > E_B$$

Hence, correct option is (a).

16. A *n*-type semiconductor has an electron concentration of $3 \times 10^{20}\ m^{-3}$. If the electron drift velocity is 100 m/s in an electric field of 200 V/m, the conductivity (in $\Omega^{-1} - m^{-1}$) of this material is **[GATE 2005]**

(a) 24 (b) 36 (c) 48 (d) 96

Soln. Conductivity, $\sigma = \frac{J}{E} = \frac{nev_d}{E} = \frac{3\times10^{20}\times1.6\times10^{-19}\times100}{200} = 2.4\times10 = 24\,\Omega^{-1} - m^{-1}$.

Hence, correct option is (a).

17. Density of states of free electrons moving in a solid with an energy 0.1 eV is given by $2.15\times10^{21}\ eV^{-1}\ cm^{-3}$. The density of state (in $eV^{-1}\ cm^{-3}$) for electrons moving with an energy of 0.4 eV will be **[GATE 2005]**

(a) 1.07×10^{21} (b) 1.52×10^{21} (c) 3.04×10^{21} (d) 4.3×10^{21}

Soln. The density of state of free electrons moving in a solid is proportional to square root of its energy,

$dn \propto \sqrt{E}$ ... (i)

For $E_1 = 0.1\,eV$, $dn_1 = 2.15\times10^{21}\ eV^{-1}cm^{-3}$.

For $E_2 = 0.4\,eV$, $dn_2 = ?$

From equation (i), we have $\frac{dn_1}{dn_2} = \sqrt{\frac{E_1}{E_2}}$

$$\Rightarrow \quad \frac{2.15\times10^{21}}{dn_2} = \sqrt{\frac{0.1}{0.4}} = \frac{1}{2} \quad \Rightarrow \quad dn_2 = 2\times2.15\times10^{21}\ eV^{-1}cm^{-3}$$

$$\Rightarrow \quad \boxed{dn_2 = 4.3\times10^{21}\ eV^{-1}cm^{-3}}.$$

Hence, correct option is (d).

18. The effective density of states at the conduction band edge of Ge is 1.04×10^{19} cm^{-3} at room temperature (300 K). Ge has an optical band gap of 0.66 eV. The intrinsic carrier concentration (in cm^{-3}) in Ge at room temperature (300 K) is approximately.

(a) 3×10^{10} (b) 3×10^{13} (c) 3×10^{16} (d) 6×10^{16}

Soln. The intrinsic carrier concentration

$$n_i = \sqrt{(N_C N_V)} \exp\left(-\frac{E_g}{2k_BT}\right)$$

$$= 1.04 \times 10^{19} \times \exp\left[-\frac{0.66 \times 1.6 \times 10^{-19}}{2 \times 1.38 \times 10^{-23} \times 300}\right] = 3 \times 10^{13} \text{ cm}^{-3}.$$

Hence, correct option is (b).

19. Lead has atomic weight of 207.2 amu and density of 11.35 g/cm^3.

(A) Number of atoms per cm^3 for lead is

(a) 1.1×10^{25} (b) 3.3×10^{22} (c) 1.1×10^{22} (d) 3.3×10^{25}

(B) If the energy of vacancy formation in lead is 0.55 eV/atom, the number of vacancies per cm^3 at 500 K is

(a) 3.2×10^{16} (b) 3.2×10^{19} (c) 9.5×10^{19} (d) 9.5×10^{16}

Soln. **(A)** We have, $\rho = 11.35$ g/cm^3 and atomic weight $M = 207.2$ amu **[GATE 2005]**

Now, the volume of the lead can be calculated by

$$\text{Volume } (V) = \frac{\text{mass } (M)}{\text{density } (\rho)} = \frac{207.2 \text{ amu}}{11.35 \text{ g/cm}^3}$$

There are 6.023×10^{23} atoms present in 207.2 amu of lead and the volume is $\frac{207.2}{11.35} \frac{\text{amu}}{\text{g/cm}^3}$

$$\text{Therefore, number of atoms per cm}^3 = \frac{6.023 \times 10^{23} \times 11.35}{207.2} = 0.3299 \times 10^{23} \text{ atom/cm}^3$$

$$= 3.3 \times 10^{22} \text{ atom/cm}^3$$

Hence, correct option is (b).

(B) Number of atoms per cm^3 $(n) = 3.3 \times 10^{22}$ atoms/cm^3

Energy of vancancy formation $(E_V) = 0.55$ eV and temperature $(T) = 500$ K

$$\text{The number of vacancies per cm}^3 = n_V = n \exp\left(-\frac{E_V}{k_BT}\right) = 3.3 \times 10^{22} \exp\left(\frac{-0.55}{8.62 \times 10^{-5} \times 500}\right)$$

$$= 3.3 \times 10^{22} \exp(-12.75) = 9.577 \times 10^{16} \text{ vacancies/cm}^3$$

Hence, correct option is (d).

20. Which one of the following is not correct statement about semiconductors? **[GATE 2006]**

(a) The electrons and holes have different mobilities in a semiconductor.

(b) In an n-type semiconductor, the Fermi-level lies closer to the conduction band edge.

(c) silicon is a direct band gap semiconductor.

(d) silicon is an indirect band gap semiconductor.

Soln. Silicon is an indirect band gap semiconductor.

Hence, correct option is (c).

21. In a crystal of N primitive cells, each cell contains two monovalent atoms. The highest occupied energy band of the crystal is **[GATE 2006]**

(a) one fourth filled (b) two third filled (c) half filled (d) completely filled

Soln. The highest occupied energy band of the crystal is half filled.
Hence, correct option is (c).

22. An extrinsic semiconductor sample of cross-section A and length L is doped in such a way that the doping concentration varies as $N_D(x) = N_0 \exp\left(-\frac{x}{L}\right)$; where N_0 is a constant. Assume that the mobility μ of the majority carriers remain constant. The resistance R of the sample is given by

(a) $R = \frac{L}{A\,\mu e\,N_0}[\exp(1.0) - 1]$ (b) $R = \frac{L}{\mu e\,N_0}[\exp(1.0) - 1]$

(c) $R = \frac{L}{A\,\mu e\,N_0}[\exp(-1.0) - 1]$ (d) $R = \frac{L}{A\,\mu e\,N_0}$

Soln. Here, cross-section area $= A$, length $= L$ **[GATE 2007]**

$N_D(x) = N_0 \exp\left(-\frac{x}{L}\right)$, where $N_0 = N_D(0)$, mobility (μ) is constant.

At $x = 0$, $N_D(0) = N_0 \exp\left(-\frac{0}{L}\right) = N_0$

At $x = L$, $N_D(L) = N_0 \exp\left(-\frac{L}{L}\right) = N_0 \exp(-1)$

$\therefore\ R = \rho\left(\frac{L}{A}\right)$; Resistivity $(\rho) = \left(\frac{N_D(L) - N_D(0)}{\mu_e N_0^2}\right) = \frac{N_0[\exp(-1) - 0]}{\mu_e N_0^2}$

$\therefore\ R = \frac{L}{A} \cdot N_0\left(\frac{\exp(-1) - 1}{\mu_e N_0^2}\right) \Rightarrow R = \frac{L[\exp(-1) - 1]}{A\,\mu_e\,N_0}$

Hence, correct option is (c).

23. Metallic monovalent sodium crystallizes in body centered cubic structure. If the length of the unit cell is 4×10^{-8} cm, the concentration of conduction electrons in metallic sodium is **[GATE 2008]**

(a) $6.022 \times 10^{23}/\text{cm}^3$ (b) $3.125 \times 10^{22}/\text{cm}^3$

(c) $2.562 \times 10^{21}/\text{cm}^3$ (d) $1.250 \times 10^{20}/\text{cm}^3$

Soln. Unit cell of bcc structure has 2 atoms in it.
Concentration of conduction electrons

$$= \frac{2}{(a)^3} = \frac{2}{(4 \times 10^{-8})^3} = \frac{2}{64 \times 10^{-24}\,\text{cm}^3} = \frac{200}{64} \times 10^{22}/\text{cm}^3 = 3.125 \times 10^{22}/\text{cm}^3$$

Hence, correct option is (b).

24. An intrinsic semiconductor with mass of a hole m_h and mass of an electron m_e is at a finite temperature T. If the top of the valence band energy is E_V and the bottom of the conduction band energy is E_C, the fermi energy of the semiconductor is **[GATE 2008]**

(a) $E_F = \left(\frac{E_V + E_C}{2}\right) - \frac{3}{4} k_B T \, \ell n \left(\frac{m_h}{m_e}\right)$ (b) $E_F = \left(\frac{k_B T}{2}\right) + \frac{3}{4}(E_V + E_C) \, \ell n \left(\frac{m_h}{m_e}\right)$

(c) $E_F = \left(\frac{E_V + E_C}{2}\right) + \frac{3}{4} k_B T \, \ell n \left(\frac{m_h}{m_e}\right)$ (d) $E_F = \left(\frac{k_B T}{2}\right) - \frac{3}{4}(E_V + E_C) \, \ell n \left(\frac{m_h}{m_e}\right)$

Soln. The Fermi energy of the semi conductor is

$$E_F = \left(\frac{E_V + E_C}{2}\right) + k_B T - \ell n \left(\frac{N_V}{N_C}\right) = \left(\frac{E_V + E_C}{2}\right) + \frac{1}{2} k_B T \, \ell n \left[\frac{2\left(\frac{2\pi m_h k_B T}{h^2}\right)^{3/2}}{2\left(\frac{2\pi m_e k_B T}{h^2}\right)^{3/2}}\right]$$

$$\Rightarrow \quad E_F = \left(\frac{E_V + E_C}{2}\right) + \frac{3}{4} k_B T \, \ell n \left(\frac{m_h}{m_e}\right)$$

Hence, correct option is (c).

25. The order of magnitude of the energy gap of a typical semiconductor is **[GATE 2011]**

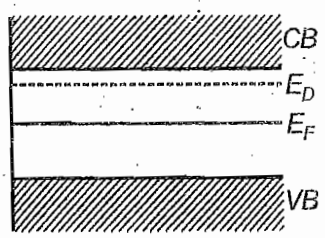
(a) 1 MeV (b) 1 keV (c) 1 eV (d) 1 meV

Soln. Energy band gap for $Si = 0.6$ eV and for $Ge = 1.1$ eV. Therefore, order of magnitude of the energy gap of a typical semiconductor is $\simeq 1$ eV.

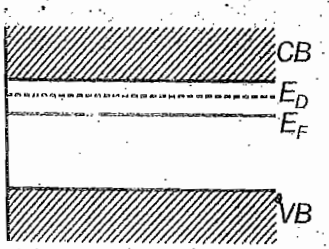
Hence, correct option is (c).

26. Identify the correct energy band diagram for silicon doped with arsenic. Here CB, VB, E_D and E_F are conduction band, valence band, impurity level and fermi level, respectively **[GATE 2012]**

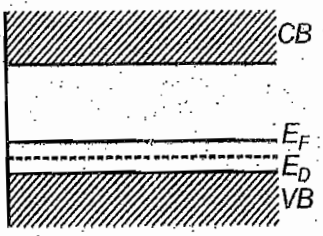
(a)



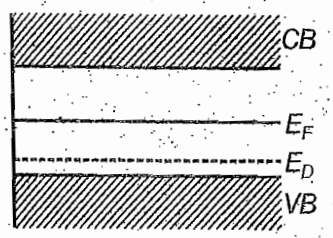
(b)



(c)



(d)



Soln. Since Si has 4 valence electrons. Arsenic is pentavalent atom. The silicon doped with arsenic will behave like an n-type semiconductor. For n-type semiconductors, the donor atoms extra electrons are at a donor energy level E_D just below the silicon conduction band ($E_C - E_D \approx 0.05$ eV). Small energy will move these electrons into conduction band. Fermi level will lie closer to conduction band just below the donor level.

Hence, correct option is (b).

27. A phosphorus doped silicon semiconductor (doping density : $10^{17}/cm^3$) is heated from 100 °C to 200 °C. Which one of the following is correct ? **[GATE 2013]**

(a) Position of Fermi-level moves towards conduction band.
(b) Position of dopant level towards conduction band.
(c) Position of Fermi-level moves towards middle of energy gap.
(d) Position of dopant level moves towards middle of energy gap.

Soln. With the increase in temperature, the concentration of minority carriers starts increasing. Eventually, a temperature is reached called the critical temperature (85 °C in case of germanium and 200 °C in case of silicon) when the number of covalent bonds that are broken is very large and the number of holes is approximately equal to the number of electrons. The extrinsic semiconductor now behaves essentially like an intrinsic semiconductor. Therefore, at 200 °C, silicon will have the Fermi-level in the middle of energy gap.
Hence, correct option is (c).

28. The donor concentration in a simple of *n*-type silicon is increased by a factor of 100. The shift in the position of the Fermi-level at 300 K, assuming the sample to be non-degenerate is_____meV. ($k_BT = 25$ meV at 300 K)

Soln. At $T = 300$ K, $k_BT = 25$ meV **[GATE 2014]**

Let initial donor concentration $= N_D^+$ and final donor concentration $= 100\ N_D^+$

$$\therefore \text{ Initial Fermi energy } (E_F)_{\text{initial}} = E_C - k_BT\ \ell n\left(\frac{N_C}{N_D^+}\right)$$

$$\text{and final Fermi energy } (E_F)_{\text{final}} = E_C - k_BT\ \ell n\left(\frac{N_C}{100\ N_D^+}\right)$$

$$\therefore \ (E_F)_{\text{final}} - (E_F)_{\text{initial}} = E_C - k_BT\ \ell n\left(\frac{N_C}{100\ N_D^+}\right) - E_C + k_BT\ \ell n\left(\frac{N_C}{N_D^+}\right)$$

$$= k_BT\ \ell n\left(\frac{N_C}{N_D^+} \times \frac{100\ N_D^+}{N_C}\right) = k_BT\ \ell n\,100 = 2 \times (k_BT) \times \ell n\,10$$

$$= 2 \times 2.303 \times 25 \text{ meV} \simeq 115 \text{ meV}$$

Hence, correct answer is 115 meV.

29. In a Hall effect experiment, the Hall voltage for an intrinsic semiconductor is negative. This is because (symbols carry usual meaning). **[GATE 2015]**

(a) $n \approx p$ (b) $n > p$ (c) $\mu_e > \mu_h$ (d) $m_e^* > m_h^*$

Soln. We know that in an intrinsic semiconductor, $n \approx p$ and $m_e^* < m_h^*$.

These relations are possible only if the mobilities of the electrons are higher than that of holes i.e., $\boxed{\mu_e > \mu_h}$.
Hence, the electrons will redistribute faster in comparison to holes. Thus, we will get negative potential instead of zero potential.
Hence, correct option is (c).

30. The band gap of an intrinsic semiconductor is $E_g = 0.72$ eV and $m_h = 6\, m_e$. At 300 K, the Fermi level with respect to the edge of the valence band (in eV) is at _____ (upto three decimal places) ($k_B T = 1.38 \times 10^{-23}$ J/K)

(Given that $E_g = E_C - E_V = 0.72$ eV). **[GATE 2015]**

Soln. The energy of Fermi level in an intrinsic semiconductor is given by

$$\Rightarrow E_F = \left(\frac{E_C + E_V}{2}\right) - \left(\frac{k_B T}{2}\right) \ell n \left(\frac{N_C}{N_V}\right)$$

$$\Rightarrow \frac{E_C + E_V}{2} = E_F + \frac{-k_B T}{2} \ell n \left(\frac{N_C}{N_V}\right)$$

$$\therefore \left(\frac{E_C - E_V}{2}\right) = \left(\frac{E_C + E_V}{2}\right) - E_V = E_F + k_B T \ell n \left(\frac{N_C}{N_V}\right) - E_V$$

$$\Rightarrow \left(\frac{E_C - E_V}{2}\right) = (E_F - E_V) + \frac{k_B T}{2} \ell n \left(\frac{N_C}{N_V}\right)$$

$$\Rightarrow E_F - E_V = \left(\frac{E_C - E_V}{2}\right) - \left(\frac{k_B T}{2}\right) \ell n \left(\frac{N_C}{N_V}\right)$$

$$= \frac{0.72 \text{ eV}}{2} - \left(\frac{1.38 \times 10^{-23} \times 300}{2}\right) \times \frac{3}{2} \times \ell n \left(\frac{m_e}{m_h}\right)$$

$$= 0.36 \text{ eV} - 1.38 \times 10^{-23} \times 150 \times \frac{3}{2} \times \ell n \left(\frac{m_e}{6\, m_e}\right)$$

$$= 0.36 \text{ eV} + \frac{1.38 \times 10^{-23}}{1.6 \times 10^{-19}} \times 150 \times \frac{3}{2} \times \ell n\, 6 \text{ eV}$$

$$= 0.36 \text{ eV} + 0.03477 \text{ eV} = 0.39477 \text{ eV} \simeq 0.395 \text{ eV}.$$

Hence, correct answer is (0.395 eV).

31. The number density of electrons in the conduction band of a semiconductor at a given temperature is 2×10^{19} m^{-3}. Upon lightly doping this semiconductor with donor impurities, the number density of conduction electrons at the same temperature become 4×10^{20} m^{-3}. The ratio of majority to minority charge carriers concentration is _____. **[GATE 2016]**

Soln. In intrinsic semiconductor, $n_i = 2 \times 10^{19}$ m^{-3}

In doped semiconductor, $n = 4 \times 10^{20}$ m^{-3}

By doping with donor impurities, the majority carriers will be electrons (n) and minority carriers will be holes (p).

From equation $n_i^2 = np$ ... (i)

$$\Rightarrow p = \frac{n_i^2}{n} = \frac{(2 \times 10^{19})^2}{4 \times 10^{20}} \text{ per m}^3$$

$$\Rightarrow p = \frac{4 \times 10^{38}}{4 \times 10^{20}} = 1 \times 10^{18} \text{ m}^{-3}$$

∴ Ratio of majority to minority charge carriers

$$\frac{n}{p} = \frac{4 \times 10^{20}}{1 \times 10^{18}} = 4 \times 10^{2} = 400$$

Hence, correct answer is (400).

32. Consider a metal which obeys the Sommerfeld modal exactly. If E_F is the Fermi energy of the metal at $T = 0\,\text{K}$ and R_H is its Hall coefficient, which of the following statements is correct? **[GATE 2016]**

(a) $R_H \propto E_F^{3/2}$ (b) $R_H \propto E_F^{2/3}$ (c) $R_H \propto E_F^{-3/2}$ (d) R_H is independent of E_F

Soln. Fermi energy can be given by $E_F = \frac{\hbar^2}{2\pi}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$ ... (i)

where, $\frac{N}{V} = n =$ electron concentration per unit volume.

$\therefore$ $\boxed{E_F \propto n^{2/3}}$ ... (ii)

and hall coefficient can be given by $R_H = \frac{1}{ne} \propto \frac{1}{n}$

$\Rightarrow$ $R_H \propto \frac{1}{n} \propto \frac{1}{E_F^{3/2}}$ $\Rightarrow$ $\boxed{R_H \propto E_F^{-3/2}}$

Hence, correct option is (c).

33. The net charge of an n-type semiconductor is

(a) positive (b) zero (c) negative (d) dependent on the dopant density **[JEST-2012]**

Soln. The net charge of an n-type semiconductor is zero. i.e., the n-type semiconductor is electrically neutral.

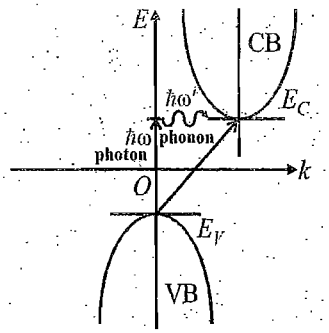
Hence, correct option is (b).

34. An electron makes a transition from the valence band to the conduction band in an indirect band gap semiconductor. Which of the following is NOT true?

(a) The energy of the electron increases (b) A phonon is involved in the process

(c) A photon is absorbed in the process (d) There is no momentum charge in the electron **[TIFR-2015]**

Soln. In the indirect band gap semiconductor, top of the valence band (E_V) and the bottom of conduction band E_C lie at different values of k.



Hence, when electrons jump from valence band to conduction band, energy and momentum both will change. Hence, option (d) is not correct for the indirect band gap semiconductor.

Hence, correct option is (d).

35. **Soln.**

36. **Soln.**

37. **Soln.**

38. **Soln.**

39. **Soln**

35. If relative density of tungeston is 18.8 gm/cm^3 and its atomic weight is 184 assuming that at room temperature there are two free electrons per atom, calculate the density of free electrons n.

Soln. Let volume = 1 cm^3.

$\therefore$ Weight = 18.8 gm for 1 cm^3 volume.

$\because$ 184 gm tungsten has 6.02×10^{23} atoms or $2\times6.02\times10^{23}$ electrons.

$\therefore$ 1 gm tungsten has $\dfrac{2\times6.02\times10^{23}}{184}$ electrons.

$\therefore$ 18.8 gm/cm^3 tungsten has $\dfrac{2\times6.02\times10^{23}}{184}\times18.8$ electrons/cm^3

Hence, number of free electrons $=1.23\times10^{23}$ electrons/cm^3.

36. Calculate the conductivity of pure silicon at room temperature when concentration of carriers is 1.6×10^{10} per cm^3. Take $\mu_n = 1500$ cm^2/v sec and $\mu_p = 500$ cm^2/v sec at room temperature.

Soln. $\sigma_i = qn_i\left(\mu_n+\mu_p\right)$

$\sigma_i = 1.6\times10^{-10}\times1.6\times10^{10}\times2000 \quad \Rightarrow \sigma_i = 5.12\times10^{-16}$ Mho/cm

37. If mobilities of electrons holes in a sample of intrinsic Ge at room temperature are 0.36 m^2/v sec and 0.17 m^2/v sec respectively. If the electron and hole densities are each equal to 2.5×10^{-19} per m^3. Calculate resistivity of Ge.

Soln. For intrinsic semiconductors

$$\sigma_i = qn_i\left(\mu_n+\mu_p\right)$$

$$\sigma_i = 1.6\times10^{19}\times2.5\times10^{-19}\times\left(0.36+0.17\right)$$

$$\sigma_i = 2.12 \text{ Simens/meter}$$

Hence, $\rho_i = 0.47\ \Omega$-meter

38. For an intrinsic silicon at 300 K, it is given that n_i value is 1.5×10^{10} per cm^3. If donor type impurity is added to extent of 1 impurity atom in 10^8 silicon atoms then calculate the value of conductivity after doping. If $\mu_n = 1300$ cm^2/v sec and $\mu_p = 500$ cm^2/v sec.

Soln. In case of Si no. of atoms/cm^3 $=5\times10^{22}$ if there is 1 donor atom per 10^8 silicon atoms.

then $N_D = \dfrac{5\times10^{22}}{10^8} = 5\times10^{14}$ atoms/cm^3

Therefore, conductivity of N-type is

$$\sigma_n = N_D\cdot q\cdot\mu_n = 5\times10^{14}\times1.6\times10^{-19}\times1300 \Rightarrow \sigma_n = 0.104 \text{ mho/cm}.$$

39. If mobility of free electron and holes in pure Ge are 0.38 and 0.18 m^2/v sec. The corresponding values for pure silicon are 0.13 and 0.05 respectively. Compare value of intrinsic resistivity for both the materials.

Soln. For Ge, $\sigma_i = n_i\ q\left(\mu_n+\mu_p\right)$

$\sigma_i = 2.5\times10^{19}\times1.6\times10^{-19}\times\left(0.56\right) \quad \Rightarrow \sigma_i = 2.24$ mho/meter

and for Si, $\sigma_i = 1.5\times10^{16}\times1.6\times10^{-19}\times0.18 \quad \Rightarrow \sigma_i = 0.432\times10^{-3}$ mho/meter

Hence, $\dfrac{\sigma_{Ge}}{\sigma_{Si}} = 5185$.

40. Calculate the number of atoms/cm^3 in case of Ge and Si.

For Ge, Atomic weight = 72.6
Density = 5.32 gm/cm^3.

For Si, Atomic weight = 28.1
Density = 2.33 gm/cm^3.

Soln. For Ge, 72.6 gm has 6.02×10^{23} atoms

5.32 gm/cm^3 has $\frac{6.02\times10^{23}}{72.6}\times5.32$ atoms/cm^3

$= 4.41\times10^{22}$ atoms/cm^3

For Si, 28.1 gm has 6.02×10^{23} atoms

2.33 gm/cm^3 has $\frac{6.02\times10^{23}}{28.1}\times2.33$ atoms/cm^3

$= 5\times10^{22}$ atoms/cm^3

PRACTICE SET

1. Calculate the probabilities for an electron state to be occupied at 20 °C if energy of state lies 0.11 eV above and 0.11 eV below Fermi-level.

2. What is occupation number at room temperature of an electron state lying 0.1 eV above Fermi-level and 0.1 eV below Fermi-level.

3. Calculate the temperature at which there is 1% probability that a state with an energy 0.5 eV above the Fermi-energy will be occupied by an electron.

4. For an intrinsic semiconductor with energy gap of 0.7 eV, calculate position of Fermi-level if $m_p = 6m_n$ at room temperature.

5. The general expression for the Fermi energy of a metal at 0°K (if n is the number of free electrons/m^3) is

   (a) $3.65 \times 10^{-19}\ n^{2/3}$ eV (b) $3.65 \times 10^{19}\ n^2$ eV
   (c) $3.65 \times 10^{19}\ n^{1/2}$ eV (d) $3.65 \times 10^{19}\ n^{3/2}$ eV

6. Fermi level is defined as

   (a) lowest filled level at 0 K (b) highest filled level at 0°C
   (c) highest filled level at 300 K (d) highest filled level at 0 K

7. The E_H, J and B are Hall field, current density and magnetic field strength, then Hall constant is given by

   (a) $R_H = \frac{E_H}{JB}$ (b) $R_H = \frac{J}{E_H B}$ (c) $R_H = \frac{BJ}{E_H}$ (d) None of these

8. The forbidden gap between valence and conduction band in metals is of the order of

   (a) 1 eV (b) 2 eV (c) 6 eV (d) very very small

9. The energy gap in semiconductors is of the order of

   (a) 0.025 eV (b) 1 eV (c) 2 eV (d) very small

10. The energy gap in the insulators is of the order of

    (a) 6 eV (b) 1 eV (c) 2 eV (d) 0.025 eV

11. In an insulator, the Fermi level is

    (a) at the bottom of conduction band (b) on top of valence band
    (c) in the middle of energy gap (d) determined by carrier concentration

12. In intrinsic germanium at room temperature the numbers of

    (a) electrons are more than holes (b) electrons and holes are equal
    (c) holes are more than electrons (d) there are no holes and electrons

13. Hall effect used to measure the sign of charge carriers, involves measurement of transverse voltage under application of

    (a) electric field only
    (b) magnetic field only
    (c) mutually perpendicular electric and magnetic fields
    (d) parallel electric and magnetic field

14. Which of the following statements concerning the electrical conductivities at room temperature of a pure copper and a pure silicon sample is not true ?
(a) If the temperature of the copper is increased, its conductivity will decrease
(b) If the temperature of the silicon is increased, its conductivity will increase
(c) The addition of an impurity in the copper always decreases its conductivity
(d) The addition of an impurity in the silicon sample always decreases its conductivity

15. Thermal conductivity k of an insulator at law temperature depends on temperature T as

(a) $K \propto T^3$ (b) $K \propto T$ (c) $K \propto T^2$ (d) $K \propto \frac{1}{T}$

ANSWER KEY

1. (0.98)	**2. (0.018, 0.98)**	**3. (1264K)**	**4. (0.385 eV)**	**5. (a)**
6. (d)	**7. (a)**	**8. (d)**	**9. (b)**	**10. (a)**
11. (c)	**12. (b)**	**13. (c)**	**14. (d)**	**15. (b)**

Chapter 9

MAGNETIC PROPERTIES OF MATERIALS

Response of substance of magnetic field:

A magnetic field can be described by either magnetic induction B (or magnetic flux density) or the field strength H. In vacuum, they are related by the equation

$$B = \mu_0 H \qquad \ldots (1)$$

where $\mu_0 = 4\pi \times 10^{-7}\ H - m^{-1}$ and is called the permeability of the free space (vacuum).

When a substance is placed in a magnetic field, it gets magnetized and hence a magnetization M(defined as the magnetic moment per unit volume, i.e. $M = \mu_m / \Delta V$) is produced in it. The magnetic induction inside the substance is given by

$$B = \mu_0 H + \mu_0 M = \mu_0 (H + M) \qquad \ldots (2)$$

where the first term on the right side of equation (2) is due to external field and the second term is due to the magnetization. For an isotropic medium, M and H are parallel vectors and are related to each other according to the relation

$$M = \chi H \qquad \ldots (3)$$

where χ is the susceptibility of the medium and is a scalar quantity. Substituting the value of M from equation (3) into equation (2), we have

$$B = \mu_0 (1 + \chi) H = \mu H \qquad \ldots (4)$$

where $\mu = \mu_0 (1 + \chi) \qquad \ldots (5)$

is known as the permeability of the medium. It is often more convenient to use the relative permeability μ_r, which is defined as

$$\mu_r = \frac{\mu}{\mu_0} = (1 + \chi) \qquad \ldots (6)$$

Magnetic susceptibility is defined as $\chi = \frac{M}{H}$.

Classification of magnetic materials:

Magnetic materials can be classified into different categories according to their χ values and the way in which these vary with the magnetic field strength and temperature. They are: (i) Diamagnetic, (ii) Paramagnetic, (iii) Ferromagnetic, (iv) Antiferromagnetic and (v) Ferrimagnetic.

The Diamagnetic property is the result of an induced magnetic moment. This arises when an atom is placed in a magnetic field. The motion of orbital electrons of the atom (analogous to a current flowing in a circuit) gets modified in such a way that weak magnetic moment opposing the field is induced. Also, if χ is negative in equation (3), the direction of magneticzation M is opposite to that of the field H. If M and H behave linearly then $\chi = \frac{M}{H}$ (for diamagnetic material)

A diamagnetic solid has a tendency to repel the magnetic lines of force due to an external applied field (figure). A superconductor which repels all the lines of force, is an example of a perfect diamagnet.

Diamagnetic substances include inert gases (helium, argon, etc). metals (bismuth, copper, zinc, gold, silver etc.), mercury, water, glass, marble and many other organic compounds. For a diamagnetic substance, the relative permeability μ_r (or the susceptitibility χ) is independent of temperature.

Unlike diamagnetism, paramagnetism and ferromagnetism are the result of intrinsic magnetic moment. Some atoms and ions do posses permanent magnetic moment. In the absence of an external field, these moments are randomly oriented with respect to one another because of thermal fluctuations and therefore the substance exhibits no net magnetic moment. However, when placed in a magnetic field, the moments tend to align along the direction of field, producing a net magnetization. When the atoms and ions are acted upon individually, with no mutual interaction between them, the effect is called paramagnetism. Since the moments line up in the direction of the field which help enhance the external field, the paramagnetic susceptibility is greater than zero. Further, because of small paramagnetic susceptibility a paramagnetic substance weakly attracts the lines of force. (Figure). As thermal energy randomizes the alignment of the dipoles, the paramagnetic susceptibility decreases with the increase of temperature.

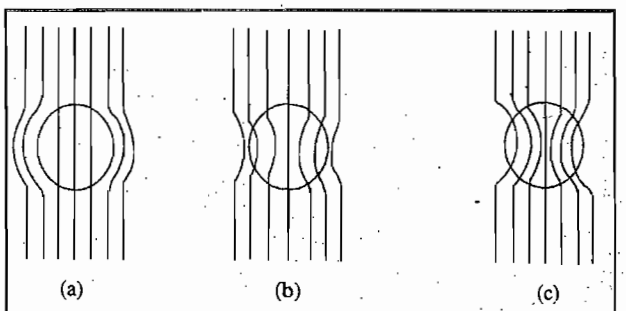


Figure: Behaviour of magnetic lines of force under applied magnetic field in (a) Diamagnet (b) Paramagneti and (c) Ferromagnet.

Paramagnetic substances include aluminium, platinum, potassium, manganese, the rare-earth elements, alkali and alkaline earth metals etc.

A ferromagnetic substance possesses permanent (spontaneous) magnetic moments even in the absence of an external magnetic field. Since, the ferromagnetic susceptibility is very large and positive, so that a ferromagnetic substance strongly attracts the lines of force (Figure). Ferromagnetism exists only below a certain temperature T_c, above which the substance becomes paramagnetic.

If M and H are not linear then $\chi = \frac{\partial M}{\partial H}$ (for ferromagnetic material).

Ferromagnetic substances include iron, cobalt, nickel and a number of alloys.

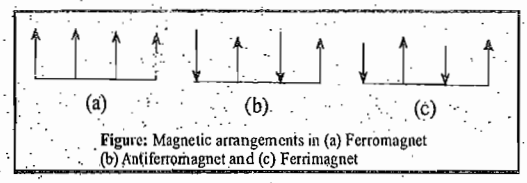


Figure: Magnetic arrangements in (a) Ferromagnet (b) Antiferromagnet and (c) Ferrimagnet

In fully magnetized state of a ferromagnet, all the dipoles are aligned in exactly the same direction (Figure). An antiferromagnetic substances has the dipoles with equal moments, but the alternate dipoles point in opposite directions (Figure). As a result, the moments balance each other and result in a zero net magnetization. Another commonly encountered substance is ferrimagnetic, the moments of which are shown in figure. In this case too, the neighbouring dipoles point in opposite directions but they are unequal. As a result, they do not completely balance each other and posses finite net magnetization.

Atomic theory of magnetism:

There are three principle sources of magnetic moment in an atom. If magnetisation M is anti-parallel to applied magnetic field then it is diamagnetic and if M is parallel to applied magnetic field then paramagnetic or ferromagnetic.

(*i*) Orbital motion of electrons

(*ii*) Spin motion electrons

(*iii*) Induce magnetic moment due to change in the orbital motion of electron on the application of external magnetic field.

In an atom, there is a nucleus about which electron do orbital motion and produce current and this constitute a magnetic dipole.

$$I = \frac{e}{T} = \frac{ev}{2\pi R}$$

Magnetic moment $\mu_m = I \cdot A = \frac{ev}{2\pi R}\pi R^2$

$$\Rightarrow \boxed{\mu_m = \frac{evR}{2}}$$

This μ_m is due to orbital motion of electron

Direction of μ_m will be decided by motion of electron.

For orbital motion of electrons, $\frac{\mu_l}{L} = \frac{e}{2m}$

Spin motion of electrons, $\frac{\mu_s}{S} = \frac{2e}{2m}$

Both orbital and spin motion of electron give paramagnetic contribution.

In an atom, we know that the electrons revolve round the nucleus in different circular orbits. Analogous to this situation let us consider an electron of mass m, having an electronic charge (–e) moving in a circular orbit of radius 'r' with a velocity v (angular velocity ω) as shown in (Figure .....) From the basic knowledge of current electricity, we know that a moving electron constitutes an electric current, i.e.

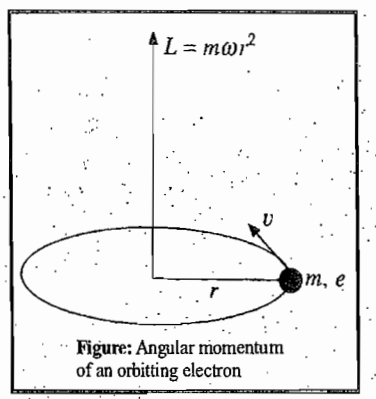


Figure: Angular momentum of an orbitting electron

$$I = \frac{dq}{dt} \text{ and } Ids = \frac{dq}{dt}ds = dq\frac{ds}{dt} = -ev \qquad \ldots (7)$$

where $dq = -e$ and $v = \frac{ds}{dt}$, the linear velocity. But for a circular orbit, $ds = 2\pi r$ and $v = \omega r$, so that

$$I \times 2\pi r = -e\omega r \qquad \Rightarrow I = -\frac{e\omega}{2\pi} \qquad \ldots (8)$$

From electromagnetic theory, it is well known that the magnetic field produced by a current, I flowing in a staionary loop of cross sectional area A at right angles to the plane of the current loop is identical with that produced by a magnetic dipole when measured at large distance (as compared to the radius of the loop). The magnitude of the magnetic moment produced by (the circular motion of the electron) such as a dipole is

$$\mu_m = I.A \qquad \ldots (9)$$

For a circular orbit $A = \pi r^2$, also substituting the value of I from equation (8) into equation (9), we obtain

$$\mu_m = -\frac{e\omega}{2\pi} \times \pi r^2$$

$$\Rightarrow \qquad \mu_m = -\frac{e\omega r^2}{2} = -\frac{em\omega r^2}{2m} = -\left(\frac{e}{2m}\right)L \qquad \ldots (10)$$

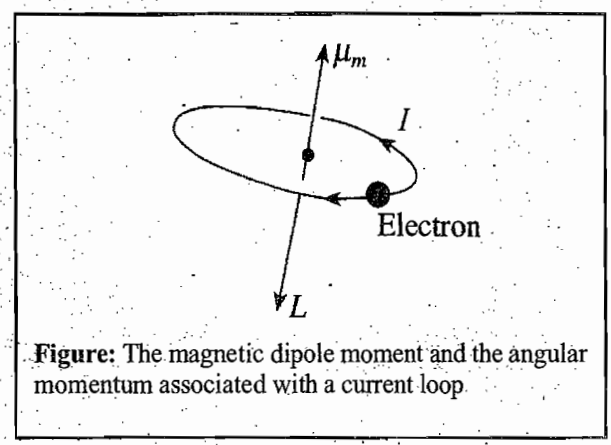


Figure: The magnetic dipole moment and the angular momentum associated with a current loop

where $L = m\omega r^2$ is the orbital angular momentum of electron and is normal to the plane of the orbital. The minus sign in equation (10) indicates that the magnetic moment μ_m is antiparallel to the angular momentum L (above figure). This equation is valid only for motion of electron and not for spin of the electron or nucleus.

The origin of permanent magnetic moments:

Permanent magnetic moments can arise from the following three different sources.

1. The orbital magnetic moment of the electrons.
2. The spin magnetic moment of the electrons, and
3. The spin magnetic moment of the nucleus.

1. The orbital magnetic moment of the electrons:

Based on the classical consideration of atomic theory of magnetism, we obtained an expression of magnetic moment (μ_m). However, quantum consideration tells us that the angular momentum vector can take only specific orientation in space when the atom is placed in an external magnetic field. Therefore, with the help of equation (10), we obtain

$$\mu_m = -\left(\frac{e}{2m}\right)L_{\ell,B} = -\left(\frac{e}{2m}\right)m_\ell \hbar = -\left(\frac{eh}{4\pi m}\right)m_\ell$$

$$\Rightarrow \qquad \mu_m = -m_\ell \mu_B \qquad \ldots (11)$$

where $\mu_B = \frac{eh}{4\pi m} = 9.27 \times 10^{-24}\ A - m^2$, and is called the Bohr magneton. It is the quantum of orbital magnetic moment and is accepted as one unit for measuring the magnetic moments of atomic systems.

In a complex atom whose shells have many electrons, the total orbital magnetic moment is determined by taking the algebraic sum of the magnetic moments of individual electrons in compliance with the rules. The moment of a completely filled shell is zero and hence an atom with paritially filled shells will have a non zero orbital magnetic moment.

2. The spin magnetic moment of the electrons:

Like orbital magnetic moment, the spin magnetic moment can be determined by substituting the value of magnetic spin angular momentum S into equation (10), we obtain

$$\mu_s = \frac{gm_B}{2} \qquad \ldots (12)$$

That is, the spin magnetic moment is half of a Bohr magneton. This is only approximately correct because equation (10) is not valid for electron spins. In fact, the magnetic moment component μ_{sz} along the field direction is given by

$$\mu_{sz} = g\left(\frac{e}{2m}\right) m_s \hbar = g\left(\frac{eh}{4\pi m}\right) m_s \qquad \ldots (13)$$

where 'g' is called the spectroscopic splitting factor or the Lande's splitting factor. For the electron spin spin g = 2.0023, i.e. the electron spin gives rise very nearly one Bohr magneton in the direction (or opposite) of an external field. The reason for the name "splitting facror" is the following. Consider an electron having no orbital motion, is placed in a magnetic field of induction B. As a result, the electron spin magnet rotates and the potential energy of the magnetic system changes. The potential energy of a magnetic dipole is then given by

$$U = -\mu B = -\mu B \cos\theta \qquad \ldots (14)$$

Now, since we know tht the magnetic spin quantum number ms can take two values, either $+\frac{1}{2}$ or $-\frac{1}{2}$. It is reasonable to assume that before the application of the field, the electron is in the higher energy state, i.e. $m_s = +\frac{1}{2}$ and after the application of the field it flips over to the lower energy, i.e. $m_s = -\frac{1}{2}$. For the state $m_s = +\frac{1}{2}$, the angular momentum vector is parallel to the field which is seen as antiparallel to the magnetic moment (angle between μ and B is 180°). Accordingly, for the state $m_s = -\frac{1}{2}$, the magnetic moment is parallel to the field (i.e. the angle between μ and B is zero). Making use of this in equation (14) and substituting μ_{sz} for μ (from equation (13), the change in the energy of the electron spin magnetic moment is:

$$\Delta U = 2|\mu_{sz}|B = g\left(\frac{eh}{4\pi m}\right)B = g\mu_B B \qquad \ldots (15)$$

Thus g determines the amount by which the original level splits up under the influence of magnetic field. This is illustrated in next figure.

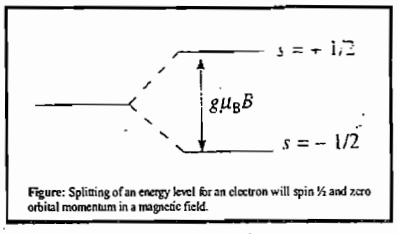


Figure: Splitting of an energy level for an electron will spin ½ and zero orbital momentum in a magnetic field.

Sometimes, the orbital angular momentum L and spin angular momentum S may be combined vectorially to get the total angular momentum J of the whole electron system of the atom. For such atoms, the spectroscopic splitting factor g is given by the Lande formula,

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad \ldots (16)$$

so that the total magnetic moment of the atomic system becomes.

$$\mu = gJ\mu_B \quad \ldots (17)$$

The values of g and J are known from the spectroscopic data and thus the total magnetic moment of a free atom or ion, in principle, can be determined.

3. The spin magnetic moment of the Nucleus:

Just like an electron, the atomic nucleus possesses intrinsic spin (called nuclear spin) and thus a magnetic moment is the associated with this. Since the nuclear mass is about 10^3 times greater than the mass of an electron, therefore the nuclear magnetic moment is approximately three orders of magnitude smaller than the magnetic moment associated with the electron. As the electron magnetic moment is expressed in the unit of Bohr magneton, similarly the nuclear magnetic moment is expressed in the unit of nuclear magneton. Anuclear magneton is defined as

$$\mu_n = \frac{eh}{4\pi m_p} = 5.05 \times 10^{-27}\ A - m^2 \quad \ldots (18)$$

where m_p is the mass of a proton.

Types of magnetic materials:

(i) Diamagnetic:

Diamagnetic effect arises due to change in the orbital motion of electron around the nucleus on the application of external magnetic field. These materials repel in the magnetic field. It is a very weak effect.

Thus, equation (2) $\Rightarrow$ $\mu H = \mu_0(H + \chi_m H)$

$$\Rightarrow \frac{\mu}{\mu_0} = 1 + \chi_m \Rightarrow \boxed{\mu_r = 1 + \chi_m}$$

Hence, $\boxed{\vec{B} = \mu_0 \mu_r \vec{H}}$

For diamagnetic material $\boxed{\mu_r < 1}$ and $\boxed{\chi_m < 0}$ i.e. negative susceptibility.

Therefore, susceptibility of diamagnetic material is negative. Diamagnetic susceptibility of a solid according to quantum mechanics is given by

$$\chi_{dia} = \frac{-\mu_0 NZ}{6m_e} e^2 < r^2 >$$

where, N is number of atoms per unit volume

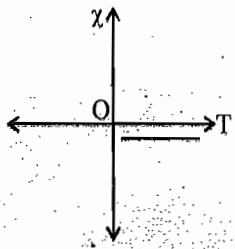
Z is atomic number, m_e is mass of the electron and $< r^2 >$ is average value of r^2 over the particular orbit. From above equation diamagnetic susceptibility is negative and independent of temperature.

For hydrogen atom ground state: $< r^2 > = \int \psi^* r^2 \psi d\tau = 3a_0^2$

Therefore, we can find out diamagnetic susceptibility of H_2.

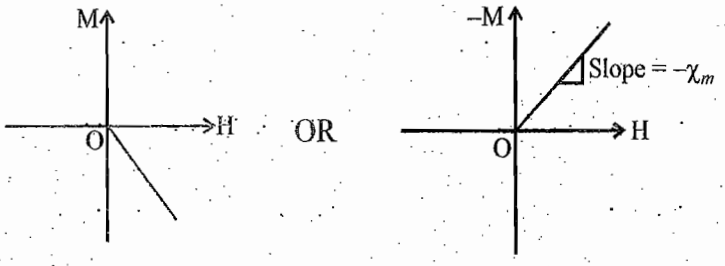
Examples: Helium, Ne, Ar, Cu, Au, Si, Ge etc.

Plot of χ versus temperature



***M-H* Curve:**

As magnetic field (H) increases magnetization (M) increases in reverse direction.



Langevin's classical theory of diamagnetism:

As we know that the diamagnetism is the occurence of negative susceptibility and the magnetization M in this case is antiparallel to the field (equation (3)). There is no electrical counterpart to the negative susceptibility, although it is vaguely analogous to the depolarization field. The negative susceptibility arises from Lenz's law which states that when the flux in an electrical circuit is changed, an induced current is set up in such a direction as to oppose the flux change. For the following discussion, a circuit will mean the circulating electron in an atom, ion or molecule at a lattice site. Let us consider the Bohr model of atom, i.e. consider an electron which revolves round a central nucleus as shown in next figure). If 'm' is the mass of the electron, –e is the charge of the electron 'r' is the radius of the orbit then in the absence of an external field the centripetal force acting on the electron due to the nucleus is given by

$$F_0 = \frac{mv^2}{r} = m\omega_0^2 r \qquad \ldots (19)$$

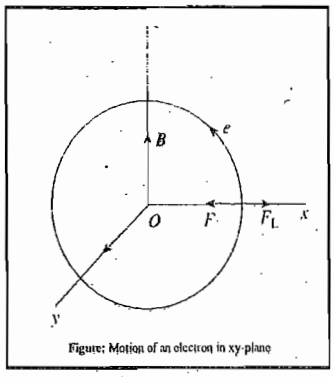


Figure: Motion of an electron in xy-plane

where $v = \omega_0 r$. When a magnetic field is applied along the z-axis (perpendicular to the xy-plane), an additional force F_L equal to the Lorentz force starts acting on the electron in a direction away from the centre. The Lorentz force is given by

$$F_L = -e(v \times B) = -eBr\omega \qquad \ldots (20)$$

where the magnetic field B is perpendicular to r. Because of the change in the net force on the electron, there is a change in the angular frequency from ω_0 to ω. The resulting equation can be written as

$$F_0 - eBr\omega = m\omega^2 r \qquad \ldots (21)$$

Substituting F_0 from equation (19) into equation (21) and solving for ω, we obtain

$$\omega^2 + \frac{eB}{m}\omega - \omega_0^2 = 0$$

So that $$\omega = \pm\left[\left(\frac{eB}{2m}\right)^2 + \omega_0^2\right]^{1/2} - \frac{eB}{2m}$$

If $\omega_0 >> \left(\frac{eB}{2m}\right)$ then $\left(\frac{eB}{2m}\right)^2$ term can be neglected, therefore,

$$\omega = \pm\omega_0 - \frac{eB}{2m} = \pm\omega_0 - \omega_L \qquad \ldots (22)$$

where the change of frequency $\omega_L = \pm\omega_0 - \frac{eB}{2m} = \pm\omega_0 - \omega_L$

where the change of frequency $\omega_L = eB/(2m)$ is called the precessional frequency or Larmour frequency. The $(\pm)$ sign on ω_0 implies that those electrons whose orbital moments are parallel to the field are slowed down by ω_L. In this case, $\omega = \omega_0 - \omega_L$. Similarly those electrons whose moments are antiparallel to the field are speeded up by the same amount. In this case, $\omega = -\omega_0 - \omega_L$.

The change in the frequency of the electronic motion as a result of the application of the magnetic field produces magnetization. Actually, in the absence of the field the electron motion being spherically symmetrical and produces no net current or flux. On the other hand, in the field, the electron's motion is no longer spherically symmetric but precesses about the field (i.e. the plane of the orbit does not remain stationary) and produces a net current I. Due to the change in frequency ω_L, the current for each electron can be written as

$$I = (\text{Charge}) \times (\text{Revolution per unit time}) = -\frac{e\omega_L}{2\pi} = -\frac{e^2 B}{4\pi m}$$

If each atom contains Z electrons then the current becomes

$$I = -\frac{Ze^2B}{4\pi m} \qquad \ldots (23)$$

Making use of equation (9), the magnetic moment could be written as

$$\mu_m = -\frac{Ze^2B}{4\pi m}\pi\bar{p}^2 \qquad \ldots (24)$$

where $\bar{p}^2$ is the mean square radius of the projection of the orbit on a plane perpendicular to the field axis. As the field is acting parallel to the z-axis, therefore,

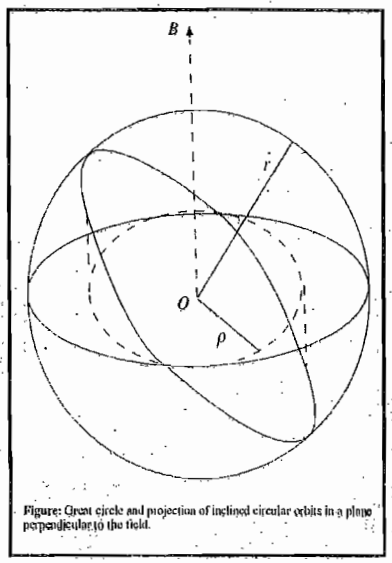


Figure: Great circle and projection of inclined circular orbits in a plane perpendicular to the field.

$$\bar{p}^2 = \bar{x}^2 + \bar{y}^2$$

The mean square distance (average radius) of the electron from the nucleus is

$$\bar{r}^2 = \bar{x}^2 + \bar{y}^2 + \bar{z}^2 \qquad \ldots (25)$$

Now, for spherically symmetric charge distribution, we have

$$\bar{x}^2 = \bar{y}^2 = \bar{z}^2$$

Here, average is used because all the electrons in an atom do not have the same effective radii, so that

$$\bar{p}^2 = \frac{2}{3}\bar{r}^2 \qquad \ldots (26)$$

This result expresses the fact that the projected area of the great circle titled with respect to the equatorial plane is less than πr^2 as shown in figure. Thus from equation (24) and (25), we obtain

$$\mu_m = -\frac{Ze^2B\pi\frac{2}{3}\bar{r}^2}{4\pi m} = -\frac{Ze^2B\bar{r}^2}{6m} \qquad \ldots (27)$$

If N is the number of atoms per unit volume, then the magnetization M is given by $M = N\mu_m$ (also making use of the fact that $B = \mu_0 H$), the diamagnetic susceptibility per unit volume is:

$$\chi_{dia} = \frac{M}{H} = -\frac{\mu_0 Ze^2 N\bar{r}^2}{6m} \qquad \ldots (28)$$

This is the classical Langevin equation for diamagnetism. From equation (28), it is clear that the diamagnetic susceptibility is proportional to N implying that the diamagnetic susceptibility depends on the size of the atom.

We also observe that χ_{dia} is proportional to $\bar{r}^2$, meaning thereby that the outer electrons make the largest contribution to the diamagnetic susceptibility.

For normal solids, we may take $N = 5\times10^{28}\ m^{-3}$, $\bar{r}^2 = 10^{-20}\ m^2$ and substituting them into equation (28) along with the values of other constant quantities, the above equation reduces to

$$\chi_{dia} \simeq Z\times10^{-7} \qquad \ldots (29)$$

This shows the temperature invariance of diamagnetic susceptibility. Diamagnetism is common to all elements, however usually it is too weak to be detected in para and ferromagnetic cases.

(ii) Paramagnetic materials:

Paramagnetism occur in those solids which have permanent magnetic moment due to spins of unpaired electrons on the application of magnetic field. These magnetic moment aligned in the direction of applied magnetic field. Hence effect is attractive type. This is strong effect as compare to diamagnetic effect. Molecular oxygen (O_2) has even number of electrons but shows paramagnetic effect (exception).

Paramagnetic suceptability of ions or atoms is given by

$\boxed{\chi_{ions} = \frac{C}{T}}$ This is known as Curie's law.

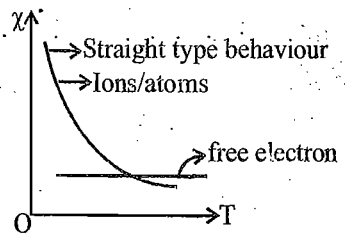
where, C is Curie constant i.e. $\chi_{ions} \propto \frac{1}{T} \Rightarrow \boxed{\chi \propto \frac{1}{T}}$

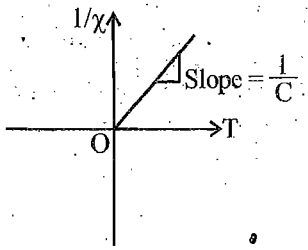
Paramagnetic suceptability of free electrons (Pauli paramagnetism) is given by

$\boxed{\chi_{\text{free electron}} = \text{Independent of temperature and positive}}$

This can not be explained by classical theory. This is explained by Quantum free electron theory.

Examples: O_2, $MnSO_4$, Mn^{+2}, Gd^{3+} etc.

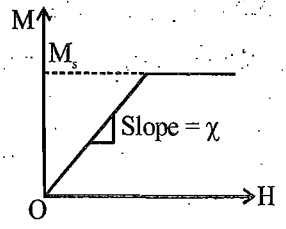




$$\chi = \frac{C}{T},\ \frac{1}{\chi} = \frac{T}{C},\ \frac{(1/\chi)}{C} = \frac{1}{C}$$

For ions / atoms

Initially M increases as H increases linearly. After a certain value of H, all the spin will aligned in the direction of applied magnetic field and M will saturate and that value of M is called M_s i.e. saturation magnetisation.



Magnetisation for a paramagnetic solid:

$$\boxed{M = NgJ\mu_B B_J(x)}$$

where, N is number of atoms per unit volume, g is Lande g-factor, J is total angular momentum, μ_B is Bohr magneton and $B_J(x)$ is Brillouin function and $\boxed{x = \frac{gJ\mu_B B}{k_B T}}$.

Special Case : For spin $\frac{1}{2}$ particles, $\boxed{M = N\mu_B \tanh\left(\frac{\mu_B B}{k_B T}\right)}$

(i) $\mu_B B \ll k_B T$ i.e. if temperature is high or strength of magnetic field is less then

Let $\frac{\mu_B B}{k_B T} = x$ so $x \ll 1$ thus, $\tanh x \simeq x = \frac{\mu_B B}{k_B T}$

Therefore, $M = N\mu_B \frac{\mu_B B}{k_B T} \Rightarrow \boxed{M = \frac{N\mu_B^2 B}{k_B T}}$

Put $B = \mu_0 H \Rightarrow M = \frac{N\mu_B^2 \mu_0 H}{k_B T}$

So, $\chi = \frac{M}{H} \Rightarrow \boxed{\chi = \frac{\mu_0 N\mu_B^2}{k_B T}}$ i.e. $\boxed{\chi \propto \frac{1}{T}}$

(ii) $\mu_B B \gg k_B T$ (temperature is low) i.e. $x \gg 1$ then $\tanh x \simeq 1$

Therefore, $\boxed{M = N\mu_B}$

This is called saturation magnetisation when all the spins are aligned in the direction of applied magnetic field.

i.e. $\boxed{M_s = N\mu_B}$

Thus magnetic susceptibility is given by

$$\boxed{\chi_s = \frac{M_s}{H} = \frac{N\mu_B}{H}}$$

From this equation it is clear that χ is independent of temperature when temperature is low or B is high.

Sources of paramagnetism:

As we know that paramagnetism is the case of a positive magnetic susceptibility. It is the magnetic analogue of the electrical orientational polarizability and is due to the permanent magnetic moment of the atoms. The direction of the magnetization is parallel to the external applied field in paramagnetic substances. Paramagnetism (positive contribution to χ) is found in:

1. Atoms, molecules and lattice defects having an odd number of electrons; that is there should be at least one

electron which does not pair. The atoms of the group I, III, V and VII of the periodic Table, gaseous nitric oxide(NO); organic free radicals such as triphenylmethyl $C(C_6H_5)_3$ and F-centres in alkali halides, satisfy this criterion.

2. Free atoms with unfilled innershell: transition elements (Z = 57–72) and (Z = 91 –102), rare earth and actinite elements have atoms with unfilled inner shells.
3. A few compounds with an even number of electrons including molecular oxygen and organic biradicals.
4. Metals: The electrons in a metal are considered to be free like molecules in a gas. They tend to pair up but there are always a few unpaired electrons to produce a weak temperature independent paramagnetism known as pauli paramagnetism.

Langevin's classical theory of paramagnetism:

As has been pointed out above that the paramagnetic susceptibility is the magnetic analogue of the electrical orientational polarizability, therefore, a similar treatment may be used to calculate this. The following are the points of similarity in the two cases:

(i) There is an assembly of permanent dipoles independent of each other oriented randomly in the absence of an external field.

(ii) The potential energy of the dipoles have the same form:

$$U(\text{electrical}) = -P.E, \text{ and } U(\text{magnetic}) = -\mu_m.B$$

Thus, substituting μ_m for P and B for E, we can use the same Langevin-Debye theory to calculate the magnetization M which is given by

$$M = N\mu_m L(x) \qquad \ldots (30)$$

where $x \equiv \frac{\mu_m B}{k_B T}$ and the Langevin function $L(x)$ is :

$$L(x) = \coth x - \frac{1}{x}$$

For $x << 1, L(x) \equiv \frac{x}{3}$ as before, so that $M = \frac{N\mu_m^2 B}{3k_B T}$

$$\Rightarrow \qquad \chi = \frac{M}{H} = \frac{\mu_0 N\mu_m^2}{3k_B T} = \frac{C}{T} \qquad \ldots (31)$$

where, $C = \frac{\mu_0 N\mu_m^2}{3k_B}$ is known as Curie constant. Consequently equation (31) is known as Curie law. The susceptibility versus temperature curve is shown in figure.

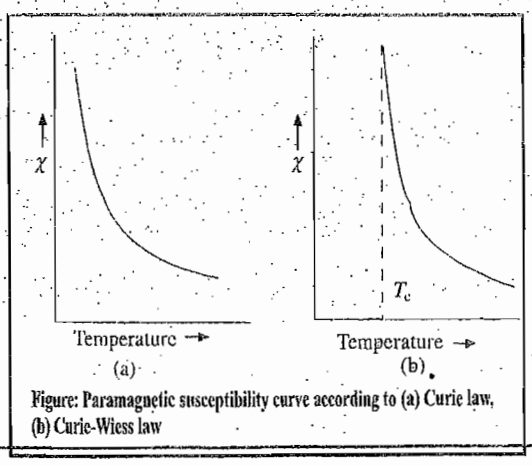


Figure: Paramagnetic susceptibility curve according to (a) Curie law, (b) Curie-Wiess law

Fundamentals of quantum theory of paramagnetism:

The Langevin's classical theory of paramagnetism is incapable of providing a consistent explanation of the magnetic phenomena resulting from the motion of electric charges. The very basis of the classical theory that all orientations of magnetic moments with respect to B are possible, is wrong according to quantum considerations. To overcome various difficulties, let us discuss the essence of quantum theory of paramagnetism based on the following basis facts:

1. For each unit of orbital angular momentum, an electron in an atom has one Bohr magneton $(\mu_B = eh/4\pi m)$ of magnetic moment associated with it. The magnetic moment is antiparallel to the angular momentum.
2. For each unit of spin angular momentum $(\hbar/2)$, there is also associated one half Bohr magneton $(\mu_B/2)$ of magnetic moment to an electron.
3. The total effective angular momentum of an electron is described as the vector sum of orbital and spin contributions, i.e.
   $$J = L + S \qquad \ldots (32)$$
4. The effective magnetic moment is given by
5. According to quantum mechanics, the magnitude of the angular momentum vector is given by $\{J(J+1)\}^{1/2}$ and not by simply J. Also there are 2J + 1 ways in which the atomic dipoles may orient relative to the magnetic field. The probability of such orientation is determined by the Boltzmann factor $\exp(-\Delta U/kT)$.

For simplicity, let us consider the atoms with L = 0. This gives g = 2, and J = S = 1/2 which in turn provide only two possible states. The lower level $(m_s = m_l = -1/2)$ corresponds to the moment parallel to the field, while the upper level corresponds to the moment opposite to the field.

Let N_1 and N_2 be the concentration of atoms in the lower and upper levels, respectively and that $N_1 + N_2 = N$ the total number of atoms. The difference of these concentrations produces a magnetization,

$$M = g\mu_B (N_1 - N_2) \qquad \ldots (33)$$

where $g\mu_B$ is the z-component of the magnetic moment when it is fully aligned with the field. These two concentrations are related by the expression.

$$\frac{N_1}{N_2} = \frac{\exp(+\Delta U/kT)}{\exp(-\Delta U/kT)} \qquad \ldots (34)$$

where $\Delta U = g\mu_B B$. Now assuming $x = g\mu_B B/kT$, we obtain

$$N_1 - N_2 = N\left(\frac{e^x - e^{-x}}{e^x + e^{-x}}\right) = N\tanh(x)$$

So, that $$M = g\mu_B (N_1 - N_2) = Ng\mu_B \tanh(x) \qquad \ldots (35)$$

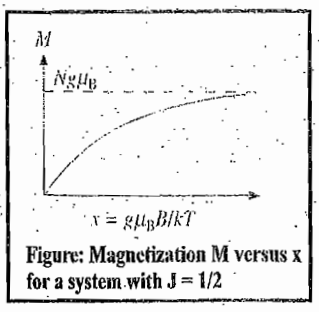


Figure: Magnetization M versus x for a system with J = 1/2

Figure shows a curve between the magnetization M and $x = g\mu_B B / kT$. At low field, M is proportional to B, but at higher fields M begins to saturate and eventually reaches a maximum value $Ng\mu_B$ when all the dipoles turn parallel to the field. Thus, for low field $x << 1$, and hence $\tanh(x) \sim x$, so that equation (35) becomes

$$M = Ng\mu_B x = \frac{N(g\mu_B)^2 B}{kT} = \frac{\mu_0 N(g\mu_B)^2 H}{kT} \qquad \ldots (36)$$

Therefore, the paramagnetic susceptibility is given by

$$\chi = \frac{M}{H} = \frac{\mu_0 N(g\mu_B)^2}{kT} \qquad \ldots (37)$$

Now, in a magnetic field, for a system of atoms with $L = 0$ and $J = S = 1/2$, the projection of magnetic moment is similar to that the spin momentum. In equation (37), μ_B is projected value of moment whereas the magnitude of the effective moment of the atom is given by

$$\mu_{eff} = 2g\mu_B \{J(J+1)\}^{1/2} = \sqrt{3}\, g\mu_B \quad \text{for} \quad S = J = \frac{1}{2}$$

$$\Rightarrow \qquad \mu_{eff}^2 = 3g^2\mu_B^2 \quad \Rightarrow g^2\mu_B^2 = \frac{\mu_{eff}^2}{3} \qquad \ldots (38)$$

Substituting this in equation (41), we have

$$\chi = \frac{\mu_0 N \mu_{eff}^2}{3kT} \qquad \ldots (39)$$

which is in agreement with the classical result. However, for $J > 1/2$ an atom with angular momentum quantum number J has $(2J+1)$ equally spaced energy levels. The magnetization is then given by

$$M = N_g J \mu_B B_J(x), \text{ with } x \equiv \frac{gJ\mu_B B}{kT} \qquad \ldots (40)$$

where the Brillouin function B_J is defined as

$$B_J(x) = \frac{(2J+1)}{2J}\coth\left(\frac{(2J+1)x}{2J}\right) - \frac{1}{2J}\coth\left(\frac{x}{2J}\right) \qquad \ldots (41)$$

where J becomes very large, the Brillouin function becomes identical to the Langevin function, i.e.

$$L(x) = \coth x - \frac{1}{x} \equiv \frac{x}{3} \qquad \ldots (42)$$

Therefore, from equation (40), the susceptibility becomes

$$\chi = \frac{\mu_0 NJ(J+1)g^2\mu_B^2}{3kT} = \frac{\mu_0 Np^2\mu_B^2}{3kT} = \frac{\mu_0 N\mu_{eff}^2}{3kT} \qquad \ldots (43)$$

where the effective moment of the atom, is now defined as $\mu_{eff} = p\mu_B$ and $p = g\{J+1\}^{1/2}$ is called the effective number of Bohr magneton for the atom.

Paramagnetism of free electrons:

According to Langevin's theory (equation 34), the paramagnetic susceptibility is inversely proportional to the temperature. However, some metals have been found to exhibit paramagnetism independent of temperature. It was W. Pauli (1927) who demonstrated that this is due to paramagnetism of free electrons (that constitute the electron gas), since they can orient only in two directions, either along the manetic field or against it.

In order to understand the existence of Pauli paramagnetism, let us recall the curve between density of states versus energy (figure) at absolute zero of temperature. That curve may be split into two parts with spins pointing in the positive z-direction and other with spin in the opposite direction, as shown in figure. In the absence of an external electric field, the distribution of electrons with spins parallel to z-direction, the energy of the spins aligned parallel to B is lowered by the amount μ_B, while the energy of the spins opposite to B is raised by the same amount (figure). As a result of this, the Fermi level for the two spin distribution shift with respect to each other and give to rise to energetically unstable situation. In order to acquire the stable configuration, the electrons lying near the Fermi level with antiparallel spins flip into the region of parallel spins until the two Fermi levels become equal again. (below Figure).

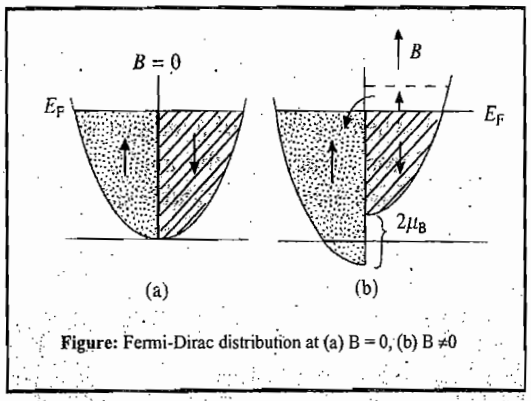


Figure: Fermi-Dirac distribution at (a) B = 0, (b) B ≠0

The number of electrons which effectively change their directions is equal to the density of states at the energy level in one of the spin distribution times the change in energy, i.e.

$$N_{eff} = \frac{1}{2} g(E_F) \mu_B B \qquad \ldots (44)$$

where the factor 1/2 is due to the fact that the density of states of one spin distribution is half of the total density of states. Thus after the application of the field, the number of electrons with spins parallel to the field is greater than the electrons with opposite spin by N_{eff}, leading to a net magnetization. Since the each flip increases the magnetization by $2\mu_B$ (from $-\mu_B$ to $+\mu_B$), the net magnetization is given by

$$M \simeq N_{eff} \times 2\mu_B = g(E_F) \mu_B^2 B \qquad \ldots (45)$$

and hence the Pauli spin susceptibility of the electron gas is:

$$\chi_p \simeq \mu_0 \mu_B^2 g(E_F) \qquad \ldots (46)$$

According to equation (46), χ_p is essentially temperature independent. This is clear from the fact that temperature has a very small effect on the Fermi-Dirac distribution of the electrons.

$$g(E_F) = \frac{3N}{2E_F}$$

So, that, $$\chi_p = \frac{3\mu_0 N \mu_B^2}{2E_F} = \frac{3\mu_0 N \mu_B^2}{2kT_F} \qquad \ldots (47)$$

where $E_F = kT_F$. This equation can be rewritten in terms of the classical susceptibility as

$$\chi_p = \frac{3}{2} \chi \frac{T}{T_F} \qquad \ldots (48)$$

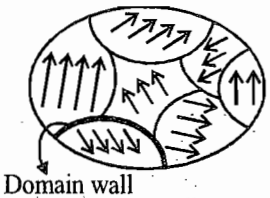
where $\chi = \frac{\mu_0 N \mu_B^2}{kT}$ for J = 1/2. Since, T_F is normally very high, χ_p is smaller than χ by about two orders of

magnitude. which is in agreement with the experimental results. In transition metals, the paramagnetic susceptibility, χ_P is exceptionally high, because $g(E_F)$ is large.

(iii) Ferromagnetic Materials: Like paramagnetism, ferromagnetism is also associated with permanent magnetic moment but ferromagnetic materials are characterize by spontaneous magnetisation (i.e. Non-zero magnetisation even in the absence of magnetic field).

Explanation of ferromagnetism can be given in terms of formation of small regions inside the solid in which magnetisation is saturated. These small regions are called domains.

Magnetic domains. Inside these domains, spins are parallel aligned and gives rise to a very large magnetic field i.e. called **Exchange field** or **Weiss field** (B_E).



Reason of formation of domain every physical process is to achieve the stability and minimize the energy.

Thickness of domain wall → few A°

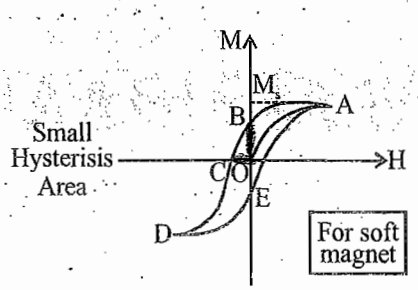
Energy quanta of spin wave is **Magnon.**

On applying H, M↑ upon saturation when H removed then M↓ but not follow the same path.

OB → Remanent magnetisation, OC → Coercive field

M–H Curve:

Sample (i) :



OC → amount of magnetic field required to destroy the coercive field.

OABCDEA → is the hysteresis loop.

This M–H curve gives the useful information about choosing the magnet for a particular type of application.

(i) Paramagnet magnet (Hard magnet)

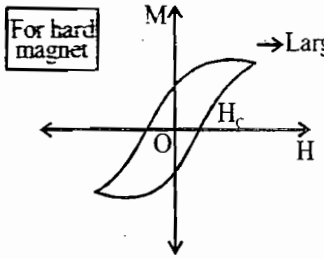
(ii) Soft magnet

SQUID (Super Conducting Quantum Interference Device) SQUID is used to measure to magnetic momentum. It is very sensitive.

VSM - Vibrating

Not much sensitive

Sample (ii):



Area of hysteresis loop = Hysteresis loss

If we want frequent magnetisation or demagnetization, hyteresis loss should be small → small area magnet will be preferred as in sample (i)

For permanent magnetisation, hysterise area should be large as in sample (ii)

H_C is coercivity.

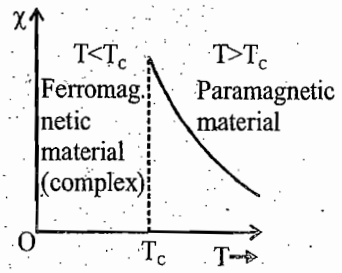
It will decide the magnet is hard or soft.

Hard magnet or paramagnet are characterise by high coercive field or by high Remanent magnetisation e.g. Steel.

Soft magnets are used in the applications where we need frequent magnetisation and demagnetisation like in transformer cores. Soft magnets are characterise by low coercive field, high Remanent magnetisation and high permeability.

Example: Soft iron and ferrites, as H_C decreases, easy will be demagnetisation / magnetisation.

Suceptability of ferromagnetic material:



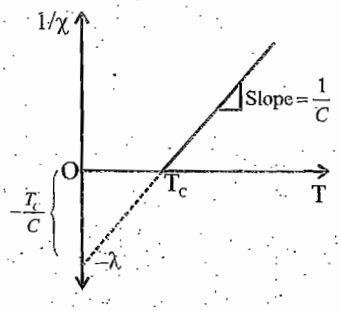
$\boxed{\chi = \frac{C}{(T - T_C)}}$ Curie-Weiss law for $T > T_C$

$T_C \rightarrow$ ferromagnetic curie temperature

For $T < T_C$, $\boxed{\chi = \text{Complex}}$

Any ferromagnetic material converts into paramagnetic material at $\boxed{T = T_C}$

$\frac{1}{\chi} = \frac{T - T_C}{C}$ $\quad$ $\frac{1}{\chi} = \frac{T}{C} - \frac{T_C}{C}$



where, C is Curie constant

$\boxed{T_C = C\lambda}$ in C.G.H. unit

T_C is Curie temperature

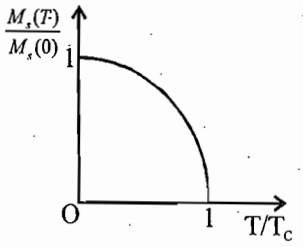
and λ is Weiss constant

Therefore, $-\frac{T_C}{C} = -\lambda$.

Temperature dependance of spontaneous magnetisation:

$$\frac{\Delta M_s}{\Delta M_s(O)} = \frac{M_s(O) - M_s(T)}{M_s(O)}$$

$$\boxed{\frac{\Delta M_s}{\Delta M_s(O)} = AT^{3/2}} \Rightarrow \text{Bloch} - T^{3/2} \text{ law}$$



As T↑, $M_s(T)$↓

So $\frac{\Delta M_s}{\Delta M_s(O)}\uparrow$

As $T \to T_C$ (from below) then

$$\boxed{M \propto (T_C - T)^{\beta}} \quad \boxed{\beta = \frac{1}{2}}$$

Near critical or Curie temperature T_C:

Saturation magnetisation or spontaneous magnetisation shows the behaviour $M \propto (T_C - T)^{1/2}$

As $T \to T_C$ (from above) then

$$\boxed{\chi \propto (T - T_C)^{\gamma}} \quad \boxed{\gamma = -1}$$

$\chi \propto (T - T_C)^{\gamma}$

At $T = T_C$ there is a discontinuity i.e. suceptability suffer a discontinuity.

Ferromagnetism:

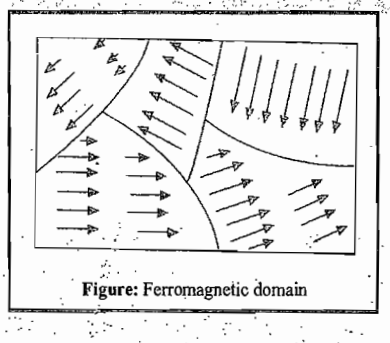


Figure: Ferromagnetic domain

In general, when we speak of a magnet we actually mean a ferromagnet. For example, consider a piece of iron, which has the ability to pick up other pieces of iron towards it, possesses permanent magnetic moments and is said to be a permanent magnet. Thus, ferromagnetism is the existence of magnetization even in th absence of the external magnetic field. Phenomenonlogically, it is the magnetic analogue of ferroelectricity. Some of the experimentally observed facts are:

1. Magnetization M increases when an external field is applied to the specimen. Moreover, the relationship between magnetization M and applied field H is nonlinear and shows hysteresis effect similar to that shown by polarization P and the electric field E.
2. The strong magnetism is found to disappear at a critical temperature (Tc), the specimen becomes demag-

netized, behaves like a paramagnet and shows magnetic effects only when an external field is applied.

3. Ferromagnetic materials are made up of large number of 'domains' (each domain contains about 10^9 – 10^{15} atoms), which are spontaneously magnetized. The magnitude of spontaneous magnetization(referse to a single domain) of the specimen is determined by the vector sum of the magnetic moments of the individual domains (Figure).
4. Within a given domain, all the dipoles (spins) are aligned in the same direction, so that magnetization is the maximum possible value for a given material and temperature.

The weiss molecular (Exchange) field:

In order to explain the spontaneous magnetization of a ferromagnetic material, Weiss (1907) assumed that there exists an internal molecular field (also called exchange field H_{ex}) acting on a given dipole and is given by

$$H_{ex} = H + \lambda M \qquad \ldots (49)$$

where λ is called Weiss constant (it is independent of temperature) and H is applied field. In a ferromagnet the Curie law holds for exchange field as well. Therefore,

$$\frac{M}{H_{ex}} = \frac{C}{T} \qquad \ldots (50)$$

Simplifying the equation (53) and (54), we have

$$M = \frac{CH}{T - C\lambda} \qquad \ldots (51)$$

Therefore, the ferromagnetic susceptibility becomes,

$$\chi = \frac{M}{H} = \frac{C}{T - C\lambda} = \frac{C}{T - T_c} \qquad \ldots (52)$$

where $T_c = C\lambda$ is called the Curie temperature and the equation (52) is known as Curie-Weiss law. The coresponding variation of suscepbitibility with temperature is shown in figure. As long as $T \geq T_c$, this curve and the curve shown in figure are similar. However, as $T \to T_c$. Curive Weiss susceptibility tends to infinity and for $T \leq T_c$ there exists a spontaneous magnetization in the material even in the absence of an external field.

Temperature dependence of spontaneous magnetization:

As discussed above, the magnetic moments due to the orbital motion of free electrons in a metal is negligible in comparision to the spin moments. Therefore, assuming only the spin system, it is possible to determine the magnetic behaviour of a ferromagnetic material below the Curie temperature. In the absence of an external field (H = 0), equation (49) reudce to

$$H_{ex} = \lambda M \qquad \ldots (53)$$

where $M = N\bar{\mu}$ is the spontaneous magnetization at some temperature T less than T_c.

According to quantum theory of paramagnetism, the magnetization M for spin half (S = J = 1/2) is given by

$$M = N_g \mu_B \tanh(x) \qquad \ldots (54)$$

where, $x = g\mu_B B / kT \qquad \ldots (55)$

For ferromagnetic case, we must replace the field B by H_{ex} given by equation (53). Therefore,

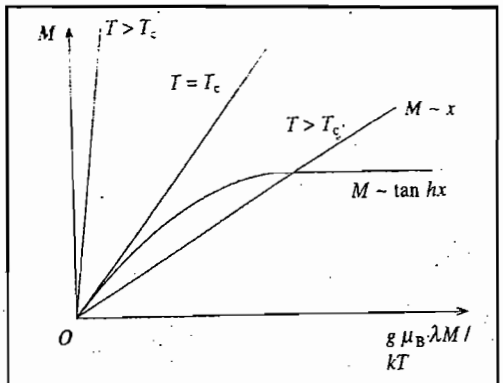


Figure: M versus x and M versus tan hx curves. The point of intersection represents spontaneous magnetization

$$x = \frac{\mu_0 g \mu_B \lambda M}{k_B T} \quad \Rightarrow \quad M = \frac{k_B T}{\mu_0 g \mu_B \lambda} x \qquad \ldots (56)$$

The equation (54) and (56) can be solved simultaenously by plotting them on M versus x graph. The value of M at a given temperature is obtained from the point of inersection of the two curves. It is clear that if T increases, the slope of the straight line also increases. For temperatures below a critical value $(T < T_c)$, the two curves intersect at a point, which gives a non vanishing spontaneous magnetization. The maximum spontaneous magnetization occurs at T = 0 K and is given by

$$M_s(0) = Ng\mu_B \qquad \ldots (57)$$

At $T = T_c$ the straight line is tangential to the hyperbolic curve (equation (57)) at the origin where the sponteaneous magnetization just reduces to zero and remains zero for all temperatues above the critical value $(T > T_c)$.

Further, at $T = T_c$, for $x << 1$, the hyperbolic function can be approximated as

$$\tanh(x) \simeq x$$

Now we have, $$\lambda = \frac{k_B T_c}{\mu_0 N (g\mu_B)^2} \qquad \ldots (58)$$

In order to describe the temperature dependence of spontaneous magnetization in a convenient manner,

$$\frac{M_s(T)}{M_s(0)} = \tanh\left(\frac{T}{T_c}\right) \qquad \ldots (59)$$

This expresses the relation between the normalized magnetization $M_s(T)/M_s(0)$ and normalized temperature T/T_c. This is called thermomagnetic equation of state for the ferromagnetic phase of materials and is shown in figure (For Ni and Gd with J = 1/2 and 7/2). This curve is universal in the sense that the ferromagnetic materials for same J value. At 0K, the magnetization is at a maximum and the normalized magnetization $M_s(T)/M_s(0)$ is unity. As the temperature is increased, thermal energy randomizes the system. As a result, the spontaneous magnetization ceases to exist above Curie temperature. This behaviour is quite similar to order-disorder transition in binary alloys in which an ordered array of atoms at low temperature, gradually loses its orderedness with increasing temperature and eventually becomes completely disorderd at the transition temperature.

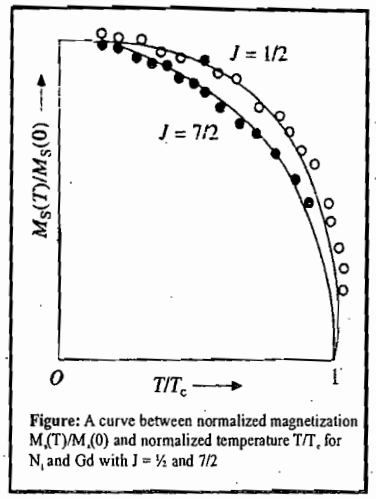


Figure: A curve between normalized magnetization $M_s(T)/M_s(0)$ and normalized temperature T/T_c for N_i and Gd with J = ½ and 7/2

Magnon:

It is a energy quanta of spin wave. Magnon is a boson. Magnon dispersion relation versus k is determined by the neutron diffraction. Magnon in ferromagnetic solid, follows $\boxed{\omega \propto k^2}$ relationship. This is not linear, this is parabolic in k.

Specific heat for a boson following quadratic relationship then in 3-dimensions, $\boxed{C_V \propto T^{3/2}}$

If boson follows linear relationship then in 3-dimensions $\boxed{C_V \propto T^3}$.

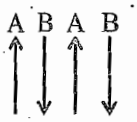
Magnon in ferromagnetic, $C_V \propto T^{3/2}$ {Magnon follow quadratic relation inside the solid in ferromagnetic}

Magnon in antiferromagnetic, $C_V \propto T^3$

Density of states, $D(E) \propto E^{1/2}$ and magnetisation, $M \propto T^{3/2}$.

(iv) Antiferromagnetism: Antiferromagnetic is characterised by antiparallel spin on neighbouring sides. Hence no spontaneous magnetisation and spin magnetic moment at side A and at side B are equal.

$m_A = m_B$



So, they cancel each other so not net magnetisation in the absence of magnetic field.

Here energy is minimized due to antiparallel spin, suceptability of antiferromagnetic material is given by

$\boxed{\chi = \frac{2C}{T + T_N'}}$ for $\boxed{T > T_N}$.

where T_N is Neel temperature

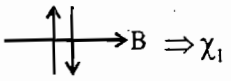
For $T < T_N$, the behaviour is antiferromagnetic and for $T > T_N$, the behaviour is paramagnetic

At $T = T_N$, behaviour of χ changes. So T_N is the reference temperature.

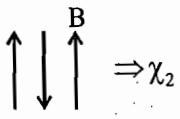
χ has two components:

(1) χ_1, B is applied perpendicular to the spin.

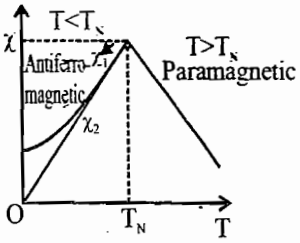
(2) χ_2, B is applied parallel to the spin.



$\Rightarrow \chi_1$



$\Rightarrow \chi_2$



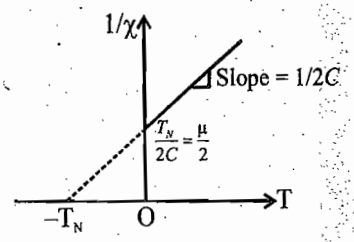
χ_1 is independent on temperature and χ_2 increases linearly with the temperature

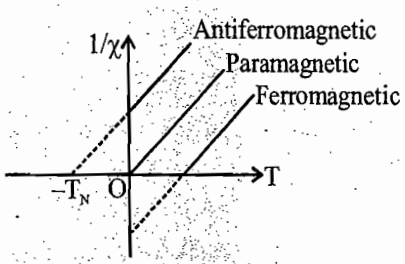
$\boxed{T_N = \mu C}$ $\{T_C = C\lambda\}$

where, C is Curie constant and μ is mean field constant.

In antiferromagnetic material, at very-very low temperature (and at very high magnetic field) there exist a very thin hysteresis loop.

At very low temperature, if magnetic field is applied and removed then spin will not remain same, that's why magnetisation is non-zero in the absence of magnetic field.

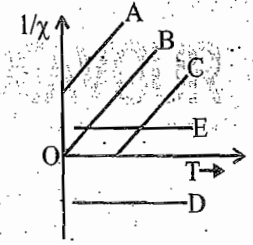




where, A corresponds to Antiferromagnetic, B corresponds to Paramagnetic, C corresponds to Ferromagnetic, D corresponds to Diamagnetic and E corresponds to Pauli paramagnetic materials.

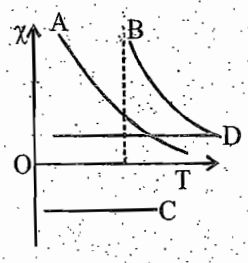
If χ is negative then $1/\chi$ will be more negative.

If χ is positive then $1/\chi$ will be more positive.



A corresponds to Paramagnetic, B corresponds to Ferromagnetic (diverge $\theta = \theta_C$), C corresponds to Diamagnetic and D corresponds to Pauli paramagnetic materials.

{In antiferromagnetic material $\theta = \theta_N \rightarrow$ Not diverge}



Examples: MnO, NiO, MnS etc.

Magnon dispersion relationship for antiferromagnetic material is linear: The ω versus k relation for magnon is given by $\boxed{\omega \propto k}$.

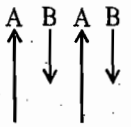
Density of states $D(E) \propto E^2$, specific heat $C_V \propto T^3$, magnetisation $M \propto T^3$.

(v) Ferrimagnetism:

Ferrimagnetism is similar to antiferromagnetism except spin magnetic moment of 2 neighbouring spin are not equal. Hence spontaneous magnetisation is observed for ferrimagnetism.

$\boxed{M_s \neq 0}$

Spins can not cancel each other.



Magnetisation at both sides A and B follows the **Curie's law**.

Example: Fe_3O_4 (ferrites)

Phase transition:

First order phase transition:

If 1st order derivative of free energy changes discontinuously at the transition point. This is called first order phase transition.

First order derivatives of energy are defined as,

(i) Entropy $S = -\left(\frac{\partial G}{\partial T}\right)_P$

(ii) Volume $V = \left(\frac{\partial G}{\partial P}\right)_T$

(iii) Magnetisation $M = \left(\frac{\partial F}{\partial B}\right)$

where, G is Gibb's free energy and F is Helmholtz free energy.

Second-order phase transition: In 2nd order phase transition second order derivative of free energy changes discontinuity at the transition point.

(i) Suceptability $x = \left(\frac{\partial M}{\partial H}\right)$

(ii) Specific heat $C_V = T\left(\frac{\partial S}{\partial T}\right)$

(iii) Isothermal compressibility $= \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)$

Examples of 2nd order phase transition:

(i) Paramagnetic to ferromagnetic or ferro $\leftrightarrow$ Para

at $\boxed{T = T_C}$ $T_C \rightarrow$ Curie temperature

(ii) Normal state $\leftrightarrow$ Super conducting state

at $T = T_C$ $T_C \rightarrow$ Critical temperature

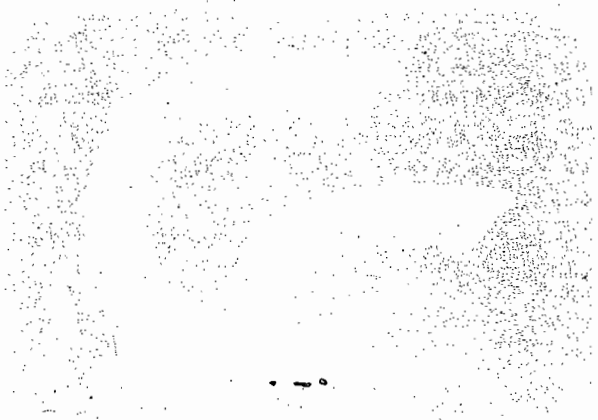
(iii) Liquid He-I $\leftrightarrow$ Liquid He-II

In 2nd order phase transition, no requirement of latent heat at the transition point.

If **100°C water** is converting into **100°C vapour**.

1st order phase transition

Water and vapour both have same energy but energy is large for vapour this comes from latent heat.



SOLVED PROBLEMS

1. A ferromagnetic material has a Curie temperature 100 K then, **[GATE 2003]**

(a) Its susceptibility is doubled when it is cooled from 300 K to 200 K.

(b) All the atomic magnets in it get oriented in the same direction above.

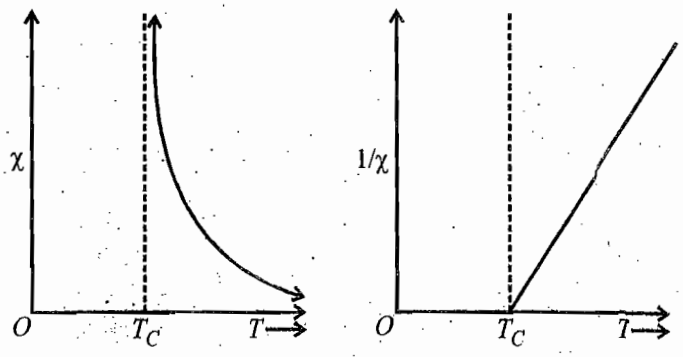
(c) The plot of inverse susceptibility versus temperature is linear with a slope (T_C).

(d) The plot of its susceptibility versus temperature is linear with an intercept T_C.

Soln. The magnetic susceptibility of a ferromagnetic material is given by

$$\chi = \frac{C}{(T - T_C)} \quad \text{... (i)}$$

Above T_C, atomic magnets will be randomly oriented and the material will become paramagnetic.



At $T = 200$ K and $T_C = 100$ K; $\chi_{200\,K} = \frac{C}{(200-100)} = \left(\frac{C}{100}\right)$ ... (ii)

At $T = 300$ K ; $\chi_{300\,K} = \frac{C}{(300-100)} = \left(\frac{C}{200}\right)$ ... (iii)

From equations (ii) and (iii), we get $\boxed{\chi_{200\,K} = 2\chi_{300\,K}}$.

Hence, correct option is (a).

2. Consider the energy E in the first Brillouin zone as a function of the magnitude of the wave vector k for a crystal of lattice constant a. Then, **[GATE 2003]**

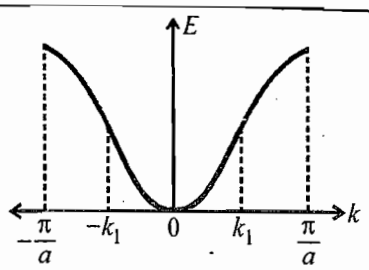
(a) the slope of E versus k is proportional to the group velocity.

(b) the slope of E versus k has its maximum value at $|k| = \frac{\pi}{a}$.

(c) the plot of E versus k will be parabolic in the inteval $\left(-\frac{\pi}{a}\right) < k < \left(\frac{\pi}{a}\right)$.

(d) the slope of E versus k is non zero for all k in the interval $\left(-\frac{\pi}{a}\right) < k < \left(\frac{\pi}{a}\right)$.

Soln. E-k diagram is represented in the figure. Also it is expressed as $E = \frac{\hbar^2 k^2}{2m}$ ... (i)



It is clear from equation (i) that the plot of E versus k will be parabolic in tle interval $\left(-\frac{\pi}{a}\right) < k < \left(\frac{\pi}{a}\right)$.

Hence, correct option is (c).

3. Which one of the following statements is true? **[GATE 2004]**

(a) Magnetic tapes are made of iron
(b) Permanent magnets are made from ferrites
(c) Ultrasonic transducers are made from quartz crystals
(d) Optoelectric devices are made from soft ferrites

Soln. The statement "ultrasonic transducers are made from quartz crystals" is only rrect statement.
Hence, correct option is (c).

4. The energy of a ferromagnet as a function of magnetization M is given by **[GATE 2005]**

$$F(M) = F_0 + 2(T - T_C)M^2 + M^4,\ F_0 > 0$$

The number of minima in the function $F(M)$ for $T > T_C$ is

(a) 0 (b) 1 (c) 3 (d

Soln. $F(M) = F_0 + 2(T - T_C)M^2 + M^4$

For minima, $\frac{\partial F(M)}{\partial M} = 0 + 2(T - T_C)\cdot 2M + 4M^3 = 0$

$\Rightarrow\ M\left((T - T_C) + M^2\right) = 0$

$\Rightarrow\ M = 0$ or $M^2 = (T_C - T) \Rightarrow M = \pm\sqrt{(T_C - T)}$ (ii)

and $\frac{\partial^2 F(M)}{\partial M^2} = 0 + 4(T - T_C) + 12M^2 = 4(T - T_C) + 12M^2$

For, $M = 0$, $\frac{\partial^2 F(M)}{\partial M^2} = 4(T - T_C) > 0$ $(\text{for } T > T_C)$

$\Rightarrow \frac{\partial^2 F(M)}{\partial M^2} > 0$, Therefore, $F(M)$ have a minima at $M = 0$

For $M = \pm\sqrt{(T_C - T)}$, $\frac{\partial^2 F(M)}{\partial M^2} = 4(T - T_C) + 12M^2 = 4(T - 12(T_C - T)$

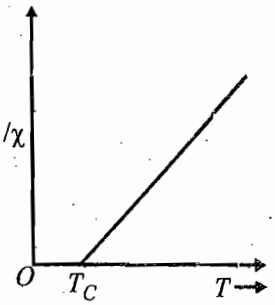
$= -8T + 8T_C < 0$ (for $T > T_C$)

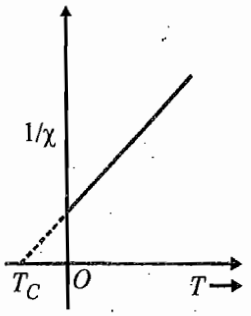
$\therefore$ $F(M)$ have a maxima at $M = \pm\sqrt{(T - T_C)}$.

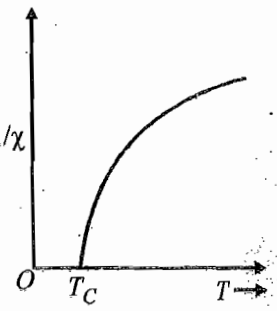
$\therefore$ Function $F(M)$ has only one minima for $T > T_C$ at $M =$

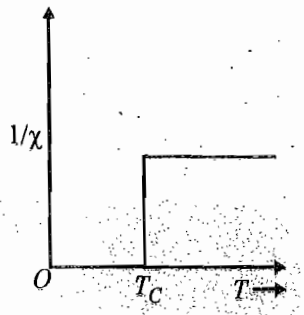
Hence, correct option is (b).

5. The plot of inverse susceptibility $(1/\chi)$ versus temperature (T) of an antiferromagnetic sample corresponds to

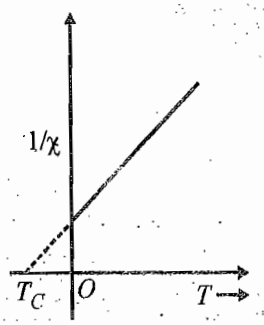
(a) 

(b) 

(c) 

(d) 

Soln. For antiferromagnetic sample, $\chi = \left(\frac{C}{T+T_C}\right) \Rightarrow \frac{1}{\chi} = \left(\frac{T+T_C}{C}\right)$



Hence, correct option is (b).

6. A system containing N non-interacting localized particles of spin-$\frac{1}{2}$ and magnetic moment μ each is kept in constant external magnetic field B and in normal equilibrium at temperature T. The magnetization of the system is

(a) $N\mu \coth\left(\frac{\mu B}{k_B T}\right)$ (b) $N\mu \tanh\left(\frac{\mu B}{k_B T}\right)$ (c) $N\mu \sinh\left(\frac{\mu B}{k_B T}\right)$ (d) $N\mu \cosh\left(\frac{\mu B}{k_B T}\right)$

Soln. The magnetization of the system is given by $M_s = N\mu \tanh\left(\frac{\mu B}{k_B T}\right)$, where $B = \mu_0 \lambda M_s$ and

$$M_s = \mu N \tanh\left(\frac{\mu_0 \mu \lambda M_s}{k_B T}\right)$$

Hence, correct option is (b).

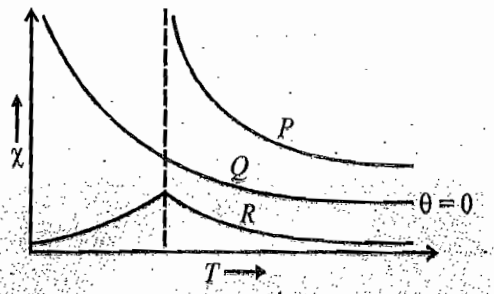
7. In insulating solid which one of the following physical phenomena is consequence of Pauli's exclusion principle?

(a) ionic conductivity (b) ferromagnetism (c) paramagnetism (d) ferroelectricity

Soln. Paramagnetism is the consequence of Pauli's exclusion principle. **[GATE 2009]**

Hence, correct option is (c).

8. The dependencies of the magnetic susceptibility (χ) of a material with temperature (T) can be represented by $\chi \propto \frac{1}{(T-\theta)}$, where θ is the Curie-Weiss temperature. The plot of magnetic susceptibility versus temperature is sketched in the figure, as curve P, Q, and R with curve Q having $\theta = 0$. Which one of the following statements is correct? **[GATE 2009]**

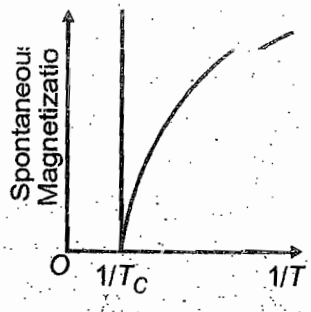


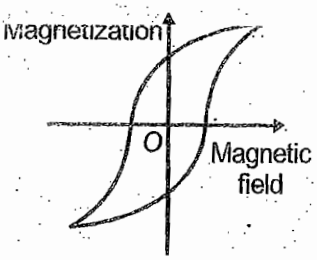
(a) curve R represents a paramagnet and Q a ferromagnet.
(b) curve Q represents a ferromagnet and P an antiferromagnet.
(c) curve R represents an antiferromagnet and Q a paramagnet.
(d) curve R represents an antiferromagnet and Q a ferromagnet.

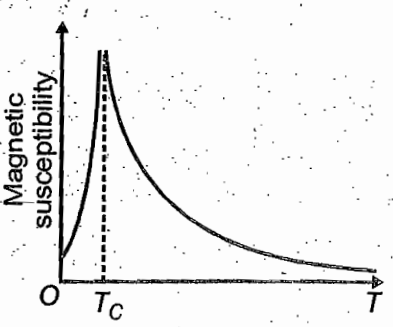
Soln. From the given figure, it is clear that curve P, Q and R represents χ versus T graphs for ferromagnetic, paramagnetic and antiferromagnetic materials respectively.

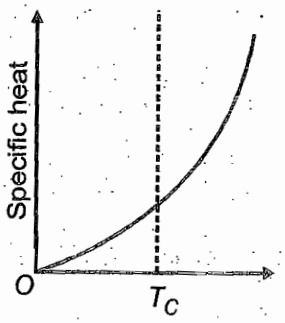
Hence, correct option is (c).

9. In an experiment involving a ferromagnetic medium, the following observations were made. Which one of the plots does not correctly represent the property of the medium? [GATE 2009]

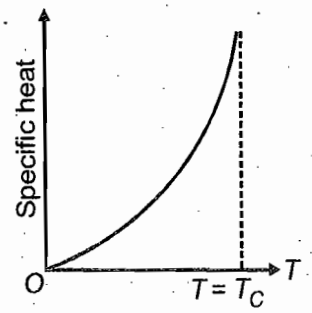
(a)


(b)


(c)


(d)


Soln. For ferromagnetic substance, the specific heat is maximum at T_c. Thus correct graph of specific heat versus T is expressed as : $C_V = -2\lambda M_s \left(\frac{\partial M_s}{\partial T}\right)$, where ; $M_s = N\mu \tan h\left(\frac{\mu_0 h\lambda M_s}{k_B T}\right)$



Thus, option (d) is not correctly shown.

Hence, correct option is (d).

10. The temperature (T) dependence of magnetic susceptibility (χ) of a ferromagnetic substance with Curie temperature (T_C) is given by **[GATE 2011]**

(a) $\frac{C}{(T-T_C)}$, for $T < T_C$

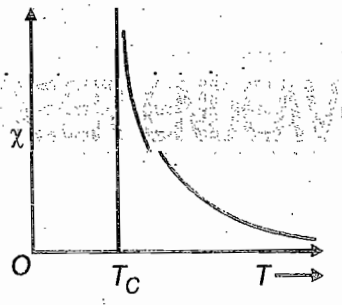
(b) $\frac{C}{(T-T_C)}$, for $T > T_C$

(c) $\frac{C}{(T+T_C)}$, for $T > T_C$

(d) $\frac{C}{(T+T_C)}$, for all temperatures

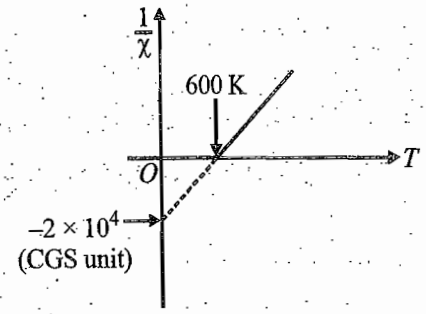
where, C is a constant.

Soln. For ferromagnetic materials, $\chi = \frac{C}{(T-T_C)}$, for $T > T_C$.



Hence, correct option is (b).

11. Inverse susceptibilty ($1/\chi$) as a function of temperature T for a materil undergoing paramagnetic to ferromagnetic transition is given in the figure, where O is the origin. The value of Curie constant C and the Weiss molecular field constant λ in CGS units, are **[GATE 2012]**



(a) $C=5\times10^{-5},\ \lambda=3\times10^{-2}$ (b) $C=3\times10^{-2},\ \lambda=5\times10^{-5}$

(c) $C=3\times10^{-2},\ \lambda=2\times10^{-4}$ (d) $C=2\times10^{-4},\ \lambda=3\times10^{-5}$

Soln. The magnetic susceptibilty of a ferromagnetic material is given by

$$\chi=\frac{C}{(T-\gamma C)} \qquad ...(i)$$

At $T=0$ K; $\chi_{T=0K}=\frac{C}{(0-\gamma C)}=\frac{C}{(-\gamma C)}=-\frac{1}{\gamma}$

$$\Rightarrow \gamma=-\frac{1}{\chi_{T=0K}}=-\left(-2\times10^{4}\right)$$

$$\Rightarrow \quad \gamma=2\times10^{4}$$

And also $T_C=\gamma C \Rightarrow C=\frac{T_C}{\gamma}=\frac{600}{2\times10^{4}}=300\times10^{-4}=3\times10^{-2}$

$$\Rightarrow \quad C=3\times10^{-2}$$

Hence, correct option is (c).

12. A solid material is found to have a temperature independent magnetic susceptibility, $\chi=C$. Which of the following statements is correct? **[GATE 2016]**

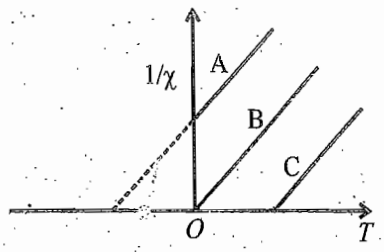
(a) If C is positive, the material is a diamagnet
(b) If C is positive, the material is a ferromagnet
(c) If C is negative, the material could be a type-I superconductor
(d) If C is positive, the material could be a type-I superconductor

Soln. Magnetic susceptibility, $\chi=C$ (independent of T) ... (i)

For type-I superconductor, the magnetic susceptibility $\chi=-1$, which is independent of temperature.

Hence, correct option is (c).

13. The magnetic susceptibility χ of three samples A, B and C is measured as a function of their absolute temperature T, leading to the graphs shown below.



From these graphs, the magnetic nature of the samples can be inferred to be

(a) A : anti-ferromagnet ; B : paramagnet ; C : ferromagnet
(b) A : diamagnet ; B : paramagnet ; C : anti-ferromagnet
(c) A : paramagnet ; B : anti-ferromagnet ; C : ferromagnet
(d) A : anti-ferromagnet ; B : diamagnet ; C : paramagnet **[TIFR-2013]**

Soln. The susceptibility of paramagnet is given by $\chi=\frac{C}{T}\Rightarrow\frac{1}{\chi}=\frac{T}{C}$ ... (i)

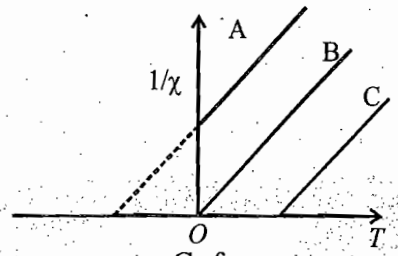
where, C is Curie constant.

The susceptibility of ferromagnet is given by $\chi = \frac{C}{(T-\theta)} \Rightarrow \frac{1}{\chi} = \left(\frac{T-\theta}{C}\right)$ ... (ii)

where, θ is Curie temperature and susceptibility of antiferromagnet is given by $\chi = \frac{C}{(T+T_N)}$, where T_N is Neel temperature.

$$\Rightarrow \frac{1}{\chi} = \left(\frac{T+T_N}{C}\right)$$

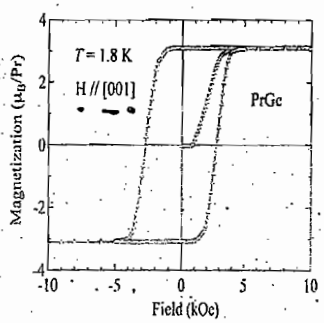
Hence plot of $\frac{1}{\chi}$ versus T for paramagnet ; ferromagnet and antiferromagnet is given by



Thus, A : anti-ferromagnet ; B : paramagnet ; C : ferromagnet

Hence, correct option is (a).

14. The Curie temperature of a single crystal of Pr Ge is known to be 41 K. The magnetization data of this sample is measured at 1.8 K for the magnetic field applied parallel to the (001) direction is shown in the figure to the left. At a temperature of 38 K, the hysteresis loop in the figure will



(a) have the same width (b) decrease in width

(c) increase in width (d) shrink to a line [TIFR-2013]

Soln. The magnetization data of the sample at $T = 1.8$ K shows a M-H loop of ferromagnetic type. After Curie temperature $T = 41$ K, this will become paramagnetic type,

At $T = 38$ K, the width of hysteresis loop decreases and above $T \triangleq 41$ K, this will shrink to a line

Hence, correct option is (c).

15. The applied magnetic field in copper is 10^6 A/m. If the magnetic susceptitibility of copper is -0.8×10^{-5}, calculate the flux density and the magnetization in copper.

Soln. Given: $H = 10^6\ A/m$, $\chi = -0.8\times10^{-5}$, $\mu_0 = 4\pi\times10^{-7}\ H/m$, B = ?, M = ? Making use of equation (3), we have

$$M = \chi H = -0.8\times10^{-5}\times10^6 = -8\ A/m$$

Further, from equation (2) we have

$$B = \mu_0(H+M) = 4\pi\times10^{-7}\left(-8+10^6\right) = 1.256\ T$$

16. Estimate the order of the diamagnetic susceptibility of copper by assuming that only one electron per atom makes the contribution. The radius of the copper atom is 1Å and the lattice parameter is 3.608Å.

Soln. Given: $r = 1\,\text{Å} = 10\text{m}$, $a = 3.608\times10^{-10}\,\text{m}$, $\chi_{dia} = ?$

We know that copper is a face centred cubic crystal, so it has 4 atoms per unit cell. The number of electrons per unit volume can be found as

$$N = \frac{n}{a^3} = \frac{4}{\left(3.608\times10^{-10}\right)^3} = 8.5\times10^{28}\,/\,\text{m}^3$$

Now making use of equation (35) and substituting the different values, we obtain

$$\chi_{dia} = -\frac{\mu_0 Ze^2 N\overline{r}^2}{6m} = -\frac{4\pi\times10^{-7}\times8.5\times10^{28}\times\left(1.6\times10^{-19}\right)^2\times10^{-20}}{6\times9.1\times10^{-31}} = -5\times10^{-6}$$

17. Approximately how large must be the magnetic induction for the orientation energy to be comparable to the thermal energy at room temperature? Assume $\mu_m = 5\mu_B$.

Soln. Given: $\mu_B = 5\beta_B$, $T = 300\text{K}$, $B = ?$

Here, the magnetic energy $= \mu_m B$ and the thermal energy kT. Now according to the question $\mu_m B \simeq kT$

$$\Rightarrow \qquad B = \frac{kT}{\mu_B} = \frac{kT}{5\mu_B} = \frac{1.38\times10^{-23}\times300}{5\times9.27\times10^{-24}} = 89.32\,\text{W/m}^2 \simeq 10^2\,\text{W/m}^2$$

18. A paramagnetic salt contains 10^{28} ions/m^3 with magnetic moment of one Bohr magneton. Calculate the paramagnetic susceptiblity and the magnetization produced in a uniform magnetic field of 10^6 A/m, at room temperature.

Soln. Given: $N = 10^{28}\,\text{ions}/\text{m}^3$, $\mu_m = \mu_B = 9.27\times10^{-24}\,\text{A/m}^2$, $H = 10^6\,\text{A/m}$,

We know that the paramagnetic susceptibility is given by

$$\chi = \frac{\mu_0 N\mu_m^2}{3kT} = \frac{4\pi\times10^{-7}\times10^{28}\times\left(9.27\times10^{-24}\right)^2}{3\times1.38\times10^{-23}\times300} = 0.87\times10^{-4}$$

Further, the magnetization is given by

$$M = \chi H = 0.87\times10^{-4}\times10^6 = 87\,\text{A/m}.$$

PRACTICE SET

1. A permanent magnet when heated above a critical temperature becomes
   (a) diamagnetic (b) ferromagnetic (c) ferrimagnetic (d) paramagnetic

2. The magnetic material in which permanent magnetic dipoles arising due to electron spins are already aligned due to bonding forces is known as
   (a) paramagnetic material (b) ferromagnetic material
   (c) ferrimagnetic material (d) diamagnetic material

3. The susceptibility of a diamagnetic material is
   (a) positive and proportional to temperature (b) negative and inversely proportional to temperature
   (c) negative and independent of temperature (d) positive and inversely proportional to temperature

4. The magnetic field intensity of a piece of iron oxide is 10^6 A/m. If the susceptibility of the material at room temperature is 1.5×10^{-3}, the magnetization produced in the material is
   (a) 1.5×10^3 A/m (b) 1.5×10^4 A/m (c) 1.5×10^5 A/m (d) 1.5×10^6 A/m

5. If the magnetic field strength in silicon is 1000 A/m and its magnetic susceptibility is -0.3×10^{-5}, its flux density will be
   (a) $1.257 \times 10^{-5} T$ (b) $1.257 \times 10^{-4} T$ (c) $1.257 \times 10^{-3} T$ (d) $1.257 \times 10^{-2} T$

6. If the number of spins in a ferromagnetic material is $3 \times 10^{28}/m^3$ and its spin magnetic moment is 3×10^{-23} A/m^2, its saturation magnetization is
   (a) 9×10^5 A/m (b) 9×10^6 A/m (c) 9×10^7 A/m (d) 9×10^8 A/m

7. The susceptibility of a piece of ferroic oxide is 1.5×10^{-3}. If the material is subjected to a magnetic field of 10^6 A/m, the flux density in the material is
   (a) 0.259 T (b) 1.259 T (c) 2.259 T (d) 3.259 T

8. Sodium metal with bcc structure has two atoms per unit cell. The radius of the sodium atom is 1.85 Å. Its diamagnetic susceptibility is
   (a) -5.18×10^{-3} (b) -5.18×10^{-4} (c) -5.18×10^{-5} (d) -5.18×10^{-6}

9. The magnetic susceptibility of a diamagnetic substance
   (a) Increases with increase in temperature
   (b) Decreases with increase in temperature
   (c) Does not change with change in temperature
   (d) First decrease with increase in temperature and then increases

10. The magnetic susceptibility of a paramagnetic substance
    (a) Increases with increase in its absolute temperature
    (b) Decreases with increase in its absolute temperature
    (c) Remains unchanged with increase in its absolute temperature
    (d) Nothing can be said

ANSWER KEY

1. (d)	2. (b)	3. (c)	4. (a)	5. (c)	6. (a)	7. (b)
8. (d)	9. (c)	10. (b)				

Chapter 10

DIELECTRICS

Dielectrics : Dielectrics are perfect insulators. In dielectrics electrons are very tightly bound to the atoms so that at ordinary temperatures they do not conduct any electric current.

Examples: Solids: glass, porcelin; gases: H_2, N_2; liquids: CH_3Cl, pure water

They are of two types.

(i) Polar dielectrics

(ii) Non-polar dielectrics

Polar dielectrics are those dielectrics whose molecules contains (are characterized by) the permanent dipole moments. Ex - H_2O, NaCl, KCl.

Non-polar dielectrics are those dielectrics whose molecules do not contain the permanent dipole moments. Ex - Solid Ar.

H_2O: Electronegativity of O is higher than H so it will have more negative charge, so it contain permanent dipole moment. It is the inherent property of molecules.

If we apply external electric field on non-polar dielectrics then it will be polarized and this polarization is called induced polarisation or induced dipole momentum.

Thus, $\vec{p}_{in} \propto \vec{E}$

$$\Rightarrow \boxed{\vec{p}_{in} = \alpha \vec{E}_{loc}} \qquad \ldots (1)$$

where, α is proportionality constant and known as polarizability of atom or molecule and $\vec{E}_{loc}$ is local electric field.

Dipole moment : If we have two equal and opposite charges $+q$ and $-q$, separated by a distance r, then the dipole moment is defined as $p = qr$. The dipole moment is directed from the negative to positive charge.

Polarization: The polarization $(\vec{P})$ is defined as the dipole moment per unit volume i.e., $\vec{P} = \frac{\vec{p}}{\Delta V}$

$$\vec{P} = \chi_e \in_0 \vec{E}_{loc} \text{ also } \vec{p}_{in} = \alpha \vec{E}_{loc} \text{ and } \vec{P} = N\vec{p}_{in} = N\alpha\vec{E}_{loc} \qquad \ldots (2)$$

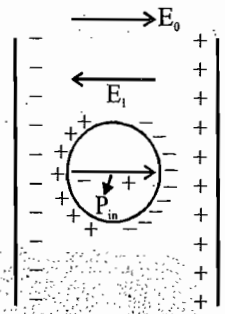
where χ_e is electric susceptibility and N is number of dipoles per unit volume.

$$\therefore \quad \chi_e = \frac{N\alpha}{\epsilon_0}$$

Since, $\epsilon_r = 1 + \chi_e \qquad \therefore \epsilon_r = 1 + \frac{N\alpha}{\epsilon_0}$

For non-polar dielectrics: If we have a large parallel plate capacitor and we fill a non-polar dielectric between its plates. Suppose external applied field is $\vec{E}_0$. Due to this $\vec{E}_0$, non-polar dielectrics will be polarized then plates occur some bound charge and electric field develop is $\vec{E}_1$ which is less than $\vec{E}_0$.

Thus, resultant electric field, $\vec{E} = \underbrace{\vec{E}_0 + \vec{E}_1}_{E_{mac}}$



Macroscopic electric field is average electric field seen between the plates.

If there is a molecule between plates then it will behave as dipole and resultant field on this molecule is different from $\vec{E}_{mac}$ and this electric field is called local field.

$$\vec{E}_{loc} = \vec{E}_0 + \vec{E}_1 + \vec{E}_2 + \vec{E}_3$$

where $\vec{E}_0$ is externally applied electric field, $\vec{E}_1$ is depolarization field, $(\vec{E}_0 + \vec{E}_1)$ is macroscopic field, $\vec{E}_2$ is electric field due to the induce charges on the surface of the cavity (polarization field).

and $\vec{E}_3$ is electric field due to all the charges inside the cavity. Resultant of all these electric fields is the local field. Take a spherical cavity out from the surrounding of molecules. This cavity is called Lorentz cavity. If the dipole is at the centre of the cavity then charges on the cavity will be symmetric about centre.

So, $\boxed{\vec{E}_3 = 0}$ (due to symmetry)

Now, $\vec{E}_{loc} = \vec{E}_0 + \vec{E}_1 + \vec{E}_2$

$\Rightarrow \quad \vec{E}_{loc} = \vec{E}_{mac} + \vec{E}_2 \qquad \left(\text{since } E_2 = \frac{\vec{P}}{3\varepsilon_0}\right)$

$\Rightarrow \quad \boxed{\vec{E}_{loc} = \vec{E}_{mac} + \frac{\vec{P}}{3\varepsilon_0}}$

If solid contains N atoms (or molecules) per unit volume, each atoms due to the application of electric field will become dipole, so there will be N dipoles.

$$\vec{P} = N\vec{p}_{in}$$

$$\Rightarrow \boxed{\vec{P} = N\alpha \vec{E}_{loc}} \quad \ldots (3)$$

From equation (2) and equation (3), we get

$$N\alpha \vec{E}_{loc} = \varepsilon_0 \chi_e \vec{E}_{mac}$$

$$\Rightarrow N\alpha \vec{E}_{loc} = \varepsilon_0 (\varepsilon_r - 1)\vec{E}_{mac} \qquad (\text{since } \chi_e = \varepsilon_r - 1)$$

$$\Rightarrow \frac{\vec{E}_{loc}}{\vec{E}_{mac}} = \frac{\varepsilon_0(\varepsilon_r - 1)}{N\alpha}$$

$$\Rightarrow \boxed{\frac{(\varepsilon_r - 1)}{(\varepsilon_r + 2)} = \frac{N\alpha}{3\varepsilon_0}}$$ where, α is electric polarizability and ε_r is dielectric constant.

This relation is known as Classius-Mossotie relation.

This is valid only for non-polar molecules.

Physical significance of Classius-Mossotie relation: Classius-Mossotie relation is a relationships between α and ε_r. α is a microscopic quantity and ε_r is macroscopic quantity (dielectric constant) because α corresponds to dipole moment and ε_r corresponds to polarisation.

For polar molecules, this equation becomes Langvein - Debye equation.

Types of polarisabilities: There are three types of polarisabilities

(i) Electronic polarisability (α_e)

(ii) Ionic polarisability (α_i)

(iii) Dipolar polarisability (α_d)

Thus total polarisability α is sum of electronic, ionic and dipolar polarisabilities.

i.e., $\alpha = \underbrace{\alpha_e + \alpha_i}_{\text{induced}} + \underbrace{\alpha_d}_{\text{Permanent}}$

CAREER ENDEAVOUR

(i) Electronic polarisability (α_e): This type of polarisability arises due to displacement of electron cloud of an atom relative to its nucleus in the presence of applied electric field.

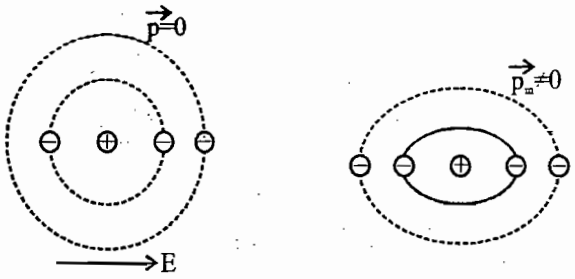
The Electronic polarisability is given by $\alpha_e = 4\pi\varepsilon_0 R^3$, where R is radius of the atom.

This type of polarisability is independent of temperature but depends on the frequency of applied electric field. The frequency dependence of α_e is given by

$$\boxed{\alpha_e = \frac{e^2}{m(\omega_0^2 - \omega^2)}}$$

where m is mass of the electron, e is electronic charge, ω_0 is natural frequency of oscillation of atom and ω is frequency of applied electric field.

Unit of α: In C.G.S. units, α has unit of volume (cm^3), and in M.K.S. units, α is measured in $F - m^2$.

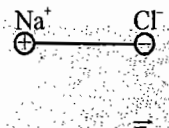


(ii) Ionic polarisability (α_i) :

This type of polarisability arises due to increase or decrease in the bond-length of ions.

This type of polarisability is independent of temperature but depends on the frequency of applied field. The ionic polarisability depends on frequency in following manner. For an ionic solid, the polarisability is given by

$$\boxed{\alpha_i = \frac{e}{\omega_0^2}\left(\frac{1}{m}+\frac{1}{M}\right)}$$



where m is mass of one ion (say Na^+),

M is mass of another ion (say Cl^-),

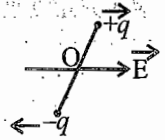
and ω_0 is natural frequency of the vibration of molecule (NaCl).

In general, $\boxed{\alpha_i \simeq \frac{\alpha_e}{10}}$.

(iii) Dipolar polarisability (α_d) :

This type of polarisability arrises due to the permanent dipole moment of the molecule. The dipolar polarisability is given by

$$\boxed{\alpha_d = \frac{p_p^2}{3k_BT}}$$



where, p_p is permanent dipole moment of the molecule, T is temperature and k_B is Boltzmann constant.

From above equation it is clear that α_d depends on both temperature and frequency of the field.

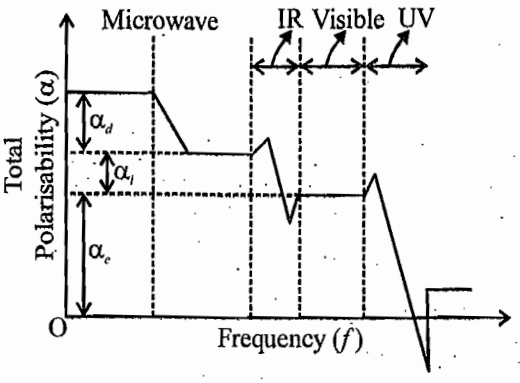
Hence total polarisability,

$\alpha = \alpha_e + \alpha_i + \alpha_d$

$$\Rightarrow \boxed{\alpha = \alpha_0 + \frac{p_p^2}{3k_BT}}$$

This relation is known as Langevin - Debye equation. This is valid for only polar molecules.

Frequency dependance of total polarisability: In visible region, total polarisation is electronic polarisation (α_e) i.e. $\alpha = \alpha_e$. Existence of $\alpha_i, \alpha_d, \alpha_e$ depends upon the relaxation time (τ). Lesser the τ, faster the response i.e. $\boxed{f \propto \frac{1}{\tau}}$.



From this figure, $\boxed{\tau_e < \tau_i < \tau_d}$

At optical frequency or visible frequency: $\boxed{\alpha = \alpha_e}$

We have $\varepsilon_r = n^2$

$$\boxed{\frac{n^2-1}{n^2+2} = \frac{N\alpha_e}{3\varepsilon_0}}$$

This relation is known as Lorentz-Lorentz relation.

Static dielectric constant from Langevin-Debye Equation:

Total polarisability $\alpha = \alpha_e + \alpha_i + \alpha_d = \alpha_e + \alpha_i + \frac{p_p^2}{3k_BT}$

Polarization : $\vec{P} = \varepsilon_0(\varepsilon_r - 1)\vec{E}_{mac} = N\alpha\vec{E}_{loc}$

If $\boxed{\vec{E}_{loc} = \vec{E}_{mac}}$

This is possible if separation between atoms and molecules is so large that there is no interaction between the dipoles like in liquid or gases.

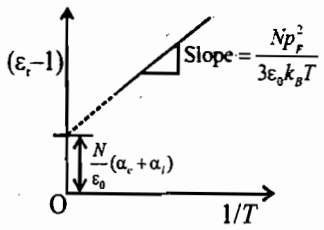
So, $\vec{P} = \varepsilon_0(\varepsilon_r - 1)\vec{E}_{mac} = N\alpha\vec{E}_{loc}$

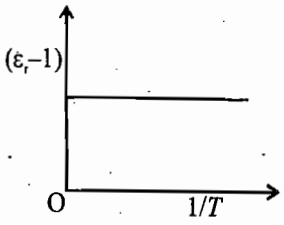
Thus, we get $\boxed{(\varepsilon_r - 1) = \frac{N}{\varepsilon_0}(\alpha_e + \alpha_i) + \frac{Np_p^2}{3\varepsilon_0 k_BT}}$

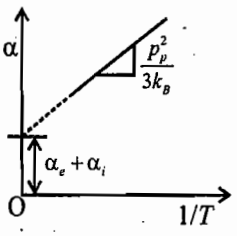
i.e., More slope $\Rightarrow$ More polar and

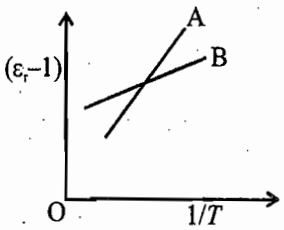
Large intercept $\Rightarrow$ More electronic and ionic polarizabilities.

If graph is flat means molecule is non-polar.





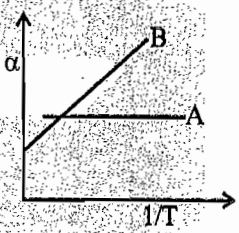




From above figure it is clear that A is more polar because of more slope.

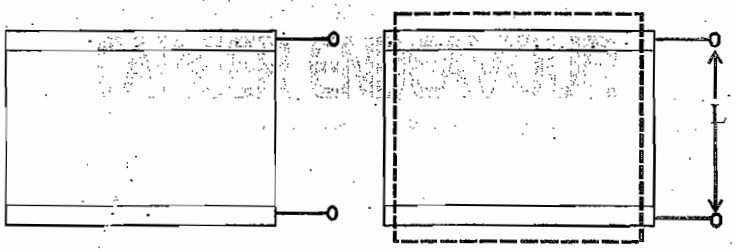
Those have permanent dipole moment are represented by B. Some of molecules that are characterized more and less polar are given below:

(i) $CH_4 \rightarrow$ A
(ii) $CO_2 \rightarrow$ A
(iii) $H_2O \rightarrow$ B
(iv) $HCl \rightarrow$ B
(v) $CO \rightarrow$ B
(vi) $CS_2 \rightarrow$ A
(vii) $SO_2 \rightarrow$ B
(viii) $NO_2 \rightarrow$ B



Piezoelectricity:

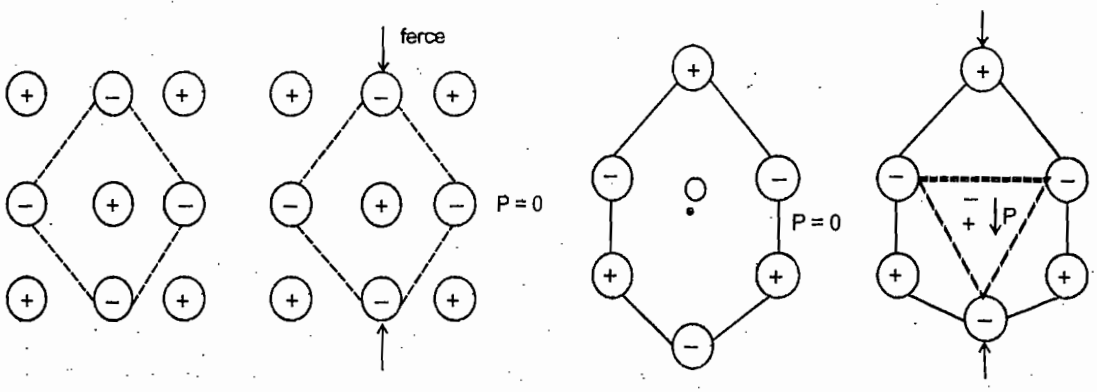
Certain crystals e.g. quartz (crystalline SiO_2) and $BaTiO_3$ become polarized when mechanically stressed. Appearance of surface charge leads to voltage difference between the two surfaces of the crystal. Same crystal also exhibit mechanical strain or distortion when they experience electric field.



Only certain crystal that exhibit no centre of symmetry, shows piezoelectricity.

Example: NaCl type has centre of symmetry.

Example: Hexagonal



Non-centro symmetric direction of polarization depends on the direction of applied stress.
Generally, an applied strees in one direction can give rise to induced polarization in other crystal direction.
Suppose, T_j is applied mechanical stress along some j direction, P_i is induced polarization along some i direction.
Two are linearly related as
$P_i = d_{ij} T_j$, where d_{ij} is piezoelectric coefficient.
The converse piezoelectric effect is that between an induced strain S_j along j direction and an applied electric field E_i along i direction.
$S_j = d_{ij} E_i$

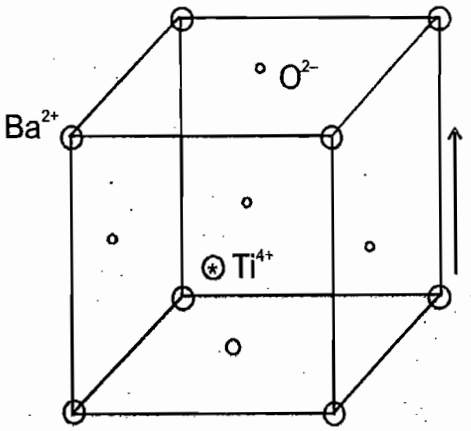
They are called transducers because they convert electrical signal, electric field to mechanical signal, strain & vice-versa used in microphones, ultrasonic transducers.
Electro-mechanical coupling factor k is defined as

$$k^2 = \frac{\text{Electrical energy converted to mechanical energy}}{\text{Input of electrical energy}}$$

$$\text{or } k^2 = \frac{\text{Mechanical energy converted to electrical energy}}{\text{Input of mechanical energy}}$$

Ferroelectric crystal:
Certain crystal are the occurrence of spontaneous polarization in certain crystal such as Barium Titanate ($BaTiO_3$). Ferroelectric crystal have a permanent polarization p as a result of spontaneous polarization. The direction of p can be defined by the application of an external field.

Pyroelectric crystal:
This material is a polar dielectric (such as $BaTiO_3$) in which a temperature change and T induces a proportional change Δp in the polarization that is $\Delta p = p\Delta T$, where p is pyroelectric coefficient of the crystal.



$p = \frac{dp}{dT}$, where p = pyrolectric coefficient

$\delta p = \varepsilon_0 (\varepsilon_0 - 1)\delta E$ is used in infrared detectors

$p \neq \varepsilon_0 (\varepsilon_r - 1) E$ rather $\Delta p = \varepsilon_0 (\varepsilon_r - 1)\Delta E$.

Δp normal to the plates changes the stored charge which is of relevance.

SOLVED PROBLEMS

1. The electronic polarizability of the Ar atom is 1.7×10^{-14} Fm^2. What is the static dielectric constant of solid Ar (below 84 K) if its density is 1.8 g cm^{-3}.

Soln. $\in_r = 1 + \frac{N\alpha_e}{\in_o}$ where $N = \frac{N_A d}{M} = \frac{6.02\times10^{23}\times1.8}{39.95} = 2.71\times10^{22}$

$$\therefore \in_r = 1 + \frac{(2.71\times10^{28})(1.7\times10^{-40})}{(8.85\times10^{-12})} = 1.52$$

Using Clausius-Mosottie equation, $\in_r = \frac{1+\frac{2N\alpha_e}{3\in_o}}{1-\frac{N\alpha_e}{3\in_o}} = \frac{1+\left(\frac{2\times(2.71\times10^{22})\times1.7\times10^{-14}}{3\times8.85\times10^{-12}}\right)}{1-\left(\frac{2.71\times10^{22}\times1.7\times10^{-14}}{3\times8.85\times10^{-12}}\right)} = 1.63$

2. Consider a pure Si Crystal that has $\in_r = 11.9$
(a) What is the electronic polarizability due to valence electron per Si atom (if one could portion the observed crystal polarization to individual atoms)?
(b) Suppose that a Si crystal sample is electroded on opposite faces and has a voltage applied across it by how much is the local field greater than the applied field?
(c) What is the Reasonant frequency of corresponding N/v = 5×10^{28} m^{-3}.

Soln. (a) $\alpha_e = \frac{3\in_o}{N}\frac{(\in_r - 1)}{(\in_r + 2)} = \frac{3(8.85\times10^{-12})}{5\times10^{28}}\frac{(11.9-1)}{(11.9+2)} = 4.17\times10^{-40} Fm^2$

(b) Local field is $E_{loc} = E + \frac{P}{3\in_o}$ $\Rightarrow P = \chi_e \in_o E = (\in_r - 1)\in_0 E$

$$E_{loc} = E + \frac{1}{3}(\in_r - 1)E \quad \Rightarrow \frac{E_{loc}}{E} = \frac{1}{3}(\in_r + 2) = 4.63$$

(c) Since polarization is due to valence electrons and there are four for Si atom, we can

Use $W_o = \left(\frac{Z_e^2}{m_e \alpha_e}\right)^{1/2} = \left[\frac{4\left(1.6\times10^{-19}\right)^2}{\left(9.1\times10^{-31}\right)\left(4.17\times10^{-14}\right)}\right]^{1/2} = 1.65\times10^{16}\, rad\ s^{-1}$ (For $\frac{\omega_o}{2\pi} = 2.6\times10^{15}\, Hz$)

3. Consider the CsCl crystal which has one Cs^+-Cl^- pair per unit cell and a lattice parametre a of 0.412 nm. The electronic polarisability of Cs^+ and Cl^- ions is 3.45×10^{-40} Fm^2 and 3.40×10^{-40} Fm^2 respectively, and the mean ionic polarisability per ion pair is 6×10^{-40} Fm^2. What is the dielectric constant at low frequencies and that at optical frequencies.

Soln. The CsCl structure has one cation Cs^+ and one anion (Cl^-) in the unit cell.
Give lattice parameters $a = 0.412 \times 10^{-9}$ m, Number of ions per unit volume in Ni is $1/a^3$.

$$\text{Number of ions per unit volume} = \frac{1}{\left(0.412\times10^{-9}\right)^3} = 1.43\times10^{28}\, m^{-3}$$

also concentration of Cations and Anions

now $$\frac{\epsilon_r - 1}{\epsilon_0 + 2} = \frac{1}{3\epsilon_0}\left[N_i\alpha_e\left(Cs^+\right) + Ni\alpha_e\left(Cl^-\right) + N_i\alpha_i\right]$$

(At low frequency) $\epsilon_r = 7.56$
(At high frequency optical frequency) ionic polarization in two sluggs

$$\frac{\epsilon_r - 1}{\epsilon_0 + 2} = \frac{1}{3\epsilon_0}\left[N_i\alpha_e\left(Cs^+\right) + Ni\alpha_e\left(Cl^-\right)\right], \quad \epsilon_r = 2.71$$

4. Consider a Piezoelectric sample in the form of a cylinder. Suppose that the piezoelectric coefficient d = 250×10^{12} mV^{-1} and $\epsilon_r = 1000$. The piezoelectric cylinder has a length of 10 mn and a diameter of 3 mm. The spinlc gap is in air and has a break down voltage of about 3.5 kV. What is the force required to spark the gap?

Soln. Induced polarization T = Stress, P = dT = $\frac{dF}{A}$

Induced polarization leads to induced surface polarization changes given by Q = AP. If C is the capacitance, then the inudced voltage is

$$V = \frac{Q}{C} = \frac{AP}{\frac{\epsilon_o\epsilon_r A}{L}} = \frac{LP}{\epsilon_0\epsilon_r} = \frac{L\left(dF/A\right)}{\epsilon_o\epsilon_r} = \frac{dLF}{\epsilon_o\epsilon_r A}$$

$$\therefore \quad F = \frac{\epsilon_o\epsilon_r AV}{dL} = \frac{\left(1000\times8.85\times10^{-12}\right)\times\left(1.5\times10^{-3}\right)^2(3500)}{\left(250\times10^{-12}\right)\left(10\times10^{-3}\right)} = 87.6\,N$$

5. Determine the percentage of ionic polarisibility in NaCl crystal which has optical index of refraction and the static dielectric constant as 1.5 and 1.6 respectively.

Soln. $$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{N\left(\alpha_e + \alpha_i\right)}{3\epsilon_0}$$

$\epsilon_r = 1.6$ and n = 1.5

$$\frac{1.6-1}{1.6+2}=\frac{N(\alpha_e+\alpha_i)}{3\epsilon_0} \quad \Rightarrow \quad \frac{1}{6}=\frac{N(\alpha_e+\alpha_i)}{3\epsilon_0} \qquad \ldots (1)$$

$$\frac{n^2-1}{n^2+2}=\frac{N\alpha_e}{3\epsilon_0} \quad \Rightarrow \quad \frac{2.25-1}{2.25+2}=\frac{N\alpha_e}{3\epsilon_0} \quad \Rightarrow \quad \frac{5}{17}=\frac{N\alpha_e}{3\epsilon_0} \qquad \ldots (2)$$

Dividing equation (1) by equation (2), we get

$$\frac{1}{6}\times\frac{17}{5}=\frac{N(\alpha_e+\alpha_i)}{3\epsilon_0}\times\frac{3\epsilon_0}{N\alpha_e} \quad \Rightarrow \quad \frac{17}{30}=1+\frac{\alpha_i}{\alpha_e}$$

$$\frac{17}{30}-1=\frac{\alpha_i}{\alpha_e} \quad \Rightarrow \frac{(\alpha_e+\alpha_i)}{\alpha_e}=\frac{17}{30} \Rightarrow \frac{\alpha_e}{(\alpha_e+\alpha_i)}=\frac{30}{17} \Rightarrow 1-\frac{\alpha_i}{(\alpha_e+\alpha_i)}=\frac{30}{17}$$

$$\Rightarrow \quad \boxed{\frac{\alpha_i}{\alpha_e+\alpha_i}\times 100=\left[1-\left(\frac{n^2-1}{n^2+2}\right)\left(\frac{\epsilon_r+2}{\epsilon_r-1}\right)\right]\times 100}$$

$$=\left[1-\left[\frac{(1.5)^2-1}{(1.5)^2+2}\right]\left(\frac{5.6+2}{5.6-2}\right)\right]\times 100=51.4\%$$

6. Infrared absorption can be observed in which of the following molecules? **[GATE 2001]**

(a) N_2 (b) O_2 (c) HCl (d) C_2

Soln. Since, we know that the infra-red absorption can be observed only on those molecules which have permanent dipole moment. In the above options, only HCl has permanent dipole moment.

Hence, correct option is (c).

7. The dielectric constant of water is 80. However its refractive index is 1.75 invalidating the expression $n=\varepsilon^{1/2}$. This is becuase **[GATE 2003]**

(a) The water molecule has a permanent dipole moment.
(b) The boiling point of water is 100°C.
(c) The two quantities are measured in different experiments.
(d) Water is transparent to visible light.

Soln. Water is a polar molecule or dielectric material. Its molecule has a permanent dipole moment that's why its dielectric constant and refractive index do not validate the expression $n=\varepsilon^{1/2}$.

Hence, correct option is (a).

8. If the static dielectric constant of NaCl is 5.6 and its optical refractive index is 1.5, the ratio of its electric polarizability to its total polarizability is **[GATE 2004]**

(a) 0.5 (b) 0.7 (c) 0.8 (d) 0.9

Soln. Clausius-Mossotti equation; $\frac{\varepsilon-1}{\varepsilon+2}=\frac{N\alpha}{3\varepsilon_0}$ ... (i)

where, α is total polarizability.

For $\varepsilon=5.6, \frac{N\alpha}{3\varepsilon_0}=\left(\frac{5.6-1}{5.6+2}\right)=\frac{4.6}{7.6}=0.605$ ... (ii)

Now, since refractive index, $n=1.5$

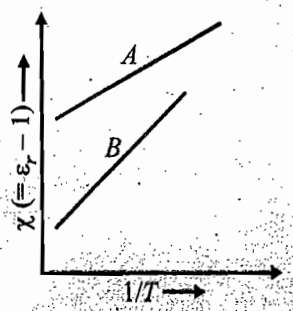
$\Rightarrow \sqrt{\varepsilon_r}=1.5 \Rightarrow \varepsilon_r=2.25$

Again from equation (i), $\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{N\alpha_e}{3\varepsilon_0} \Rightarrow \frac{N\alpha_e}{3\varepsilon_0} = \left(\frac{2.25-1}{2.25+2}\right) = 0.2941.$

$$\therefore \frac{\text{Electric polarizability}}{\text{Total polarizability}} = \frac{\alpha_e}{\alpha} = \frac{\left(\frac{N\alpha_e}{3\varepsilon_0}\right)}{\left(\frac{N\alpha}{3\varepsilon_0}\right)} = \frac{0.294}{0.605} = 0.486 \approx 0.5.$$

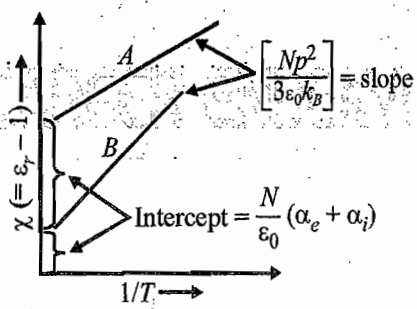
Hence, correct option is (a).

9. Two dielectric materials A and B exhibit both ionic and orientational polarizabilities. The variation of their susceptibilities $\{\chi = (\varepsilon_r - 1)\}$ with temperature (T) is shown in the figure, where ε_r is the relative dielectric constant. It can be inferred from the figure that **[GATE 2006]**



(a) A is more polar and it has a smaller value of ionic polarizability than that of B.
(b) A is more polar and it has a higher value of ionic polarizability than that of B.
(c) B is more polar and it has a higher value of ionic polarizability than that of A.
(d) B is more polar and it has a smaller value of ionic polarizability than that of A.

Soln. The susceptibility (χ) is given by $\chi = (\varepsilon_r - 1) = \frac{N}{\varepsilon_0}(\alpha_e + \alpha_i) + \left(\frac{Np^2}{3\varepsilon_0 k_B T}\right)$

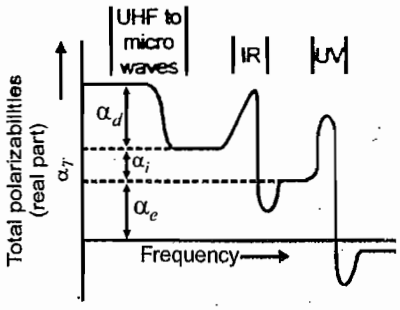


Since, slope of B > slope of A, therefore, B is more polar.
Since intercept of A is larger than B, therefore ionic polarizability of B is lesser in comparison to A.
Hence, correct option is (d).

10. The dielectric constant of a material at optical frequencies is mainly due to **[GATE 2009]**

(a) ionic polarizability
(b) electronic polarizability
(c) dipolar polarizability
(d) ionic and dipolar polarizability

Soln. The dielectric constant of a material at optical frequency is mainly due to ionic polarizability.



Hence, correct option is (a).

11. In a hydrogen atom, consider that the electronic charge is uniformly distributed in a spherical volume of radius $a(=0.5\times10^{-10}\text{ m})$ around the proton. The atom is placed in a uniform electric field $E=30\times10^{5}$ V/m. Assume that the spherical distribution of the negative charge remains undistorted under the electric field.

(A) In the equilibrium, the separation between the positive and negative charge is **[GATE 2012]**

(a) 8.66×10^{-16} m (b) 2.6×10^{-15} m (c) 2.60×10^{-16} m (d) 8.66×10^{-15} m

(B) The polarizability of the hydrogen atom in unit of $(C^2\cdot\text{m/N})$ is

(a) 2.0×10^{-40} (b) 1.4×10^{-41} (c) 1.4×10^{-40} (d) 2.0×10^{-39}

Soln. **(A)** Since, $E=\dfrac{1}{4\pi\varepsilon_0}\cdot\dfrac{P}{a^3}$

$$\Rightarrow\quad a^3=\frac{P}{4\pi\varepsilon_0 E}=\frac{qd}{4\pi\varepsilon_0 E}$$

$$\Rightarrow\quad d=\frac{4\pi\varepsilon_0 a^3 E}{q}=\frac{4\times3.14\times8.854\times(0.5\times10^{-10})^3\times30\times10^5\times10^{-12}}{1.6\times10^{-19}}=260.63\times10^{-18}\text{ m}$$

$$\Rightarrow\quad d=2.60\times10^{-16}\text{ m}.$$

Hence, correct option is (c).

(B) Since, dipole moment $(p)=q\times d=\alpha E$

$$\Rightarrow\quad \alpha=\frac{qd}{E}=\frac{1.6\times10^{-19}\times2.6\times10^{-16}}{30\times10^5}=0.139\times10^{-40}$$

$$\Rightarrow\quad \alpha=1.4\times10^{-41}.$$

Hence, correct option is (b).

PRACTICE SET

1. In a drop of water of radiius 10^{-3}m, the molecular dipoles are pointed in the same direction. If the dipole moment of the water molecule is 6×10^{-30} $C\text{-}m$, its polarization will be

   (a) 8.4×10^{-10} C/m^2 (b) 8.4×10^{-12} C/m^2 (c) 8.4×10^{-14} C/m^2 (d) 8.4×10^{-16} C/m^2

2. The relative permittivity of argon at 0°C and one atmosphere is 1.000435, the electronic polarizability of the argon atom will be

   (a) 1.43×10^{-38} Fm^2 (b) 1.43×10^{-39} Fm^2 (c) 1.43×10^{-40} Fm^2 (d) 1.43×10^{-41} Fm^2

3. A photon of wavelength 1400Å is absorbed by cold mercury vapour and two other photons are emitted. If the wavelength of one of them is 1850 Å, the wavelength of the other photon will be

   (a) 5755Å (b) 5855Å (c) 5955Å (d) 6055Å

4. Determine the % of ionic polarisability in NaCl crystal which has optical index of refraction as 1.5 and dielectric constant as 1.6.

5. Dielectric polarizability is a proportionality constant in the relation between
   (a) Electric dipole moment and local electric field
   (b) Displacement vector and local electric field
   (c) Electric dipole moment and charge density
   (d) Displacement vector and charge density

6. $\dfrac{\varepsilon_r-1}{\varepsilon_r+2}=\dfrac{N\alpha}{3\varepsilon_0}$ is

   (a) Lorentz relation (b) Einstein relation
   (c) Clausius-Mosottie relation (d) None of these

7. For ferromagnetic materials, the permeability 'μ' is

   (a) < 1 (b) = 1 (c) > 1 (d) >> 1

8. Dipole moment of a current loop is given by

   (a) niA (b) nqA (c) $\dfrac{n}{q}A$ (d) $\dfrac{nA}{i}$

   where n = numbers of turns, i = current and A = area of cross section of the loop, q = charge.

9. Electrons are emitted with zero velocty from a certain metal surface when it is exposed to a radiation of wavelength 6850Å. The work function of the metal is

   (a) 0.813 eV (b) 1.813 eV (c) 2.813 eV (d) 3.813 eV

10. When a surface of copper is irradiated by light of wavelength 1849Å, the stopping potential is found to be 2.72 volts. The threshold frequency of the metal is

    (a) 9.658×10^{12} c/s (b) 9.658×10^{13} c/s (c) 9.658×10^{14} c/s (d) 9.658×10^{15} c/s

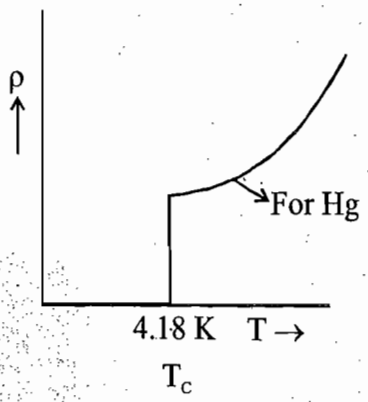
ANSWER KEY

1. (a)	**2. (c)**	**3. (a)**	**4. (51.4%)**	**5. (a)**	**6. (c)**
7. (d)	**8. (a)**	**9. (b)**	**10. (c)**		

Chapter 11

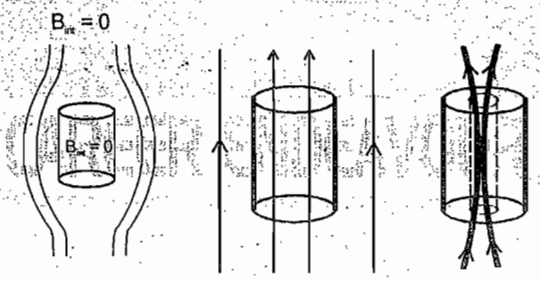
SUPERCONDUCTIVITY

In 1911, Kammerlingh Onnes discovered that the electrical resistivity of Hg (mercury) at low temperature $\simeq 4.18\,K$, vanishes (zero) suddenly. This phenomenon was given the name superconductivity. The temperature at which the resistivity disappear (in zero magnetic field) is called the transition temperature or critical temperature (T_C). The transition temperature of mercury is 4.18 K, materials which shows this phenomenon are called superconducters.



Meissner's effect:

This effect is useful to make difference between superconductor and perfect (normal) conductor. When a superconductor and a perfect conductor are placed in an external magnetic field, the magnetic line of the forces do not passes through the superconductor and they are swept away. Thus making the magnetic field (B) inside the superconductor equal to zero. While line of magnetic force passes through the perfect conductor and therefore B is not equal to zero inside the perfect conductor.



As in case of superconductor, magnetic field $B = 0$

In C.G.S. units:

$$\vec{B} = \vec{H} + 4\pi M \Rightarrow \quad \frac{M}{H} = -\frac{1}{4\pi} \Rightarrow \boxed{\chi = -\frac{1}{4\pi}}$$

In M.K.S. units:

$$\Rightarrow \quad \mu_0 (H + M) = 0$$

$$\Rightarrow \quad H + M = 0 \quad \frac{M}{H} = -1 \Rightarrow \boxed{\chi = -1}$$

where χ is magnetic succeptibility, H is magnetic field intensity and M is magnetization.

Thus the succeptibility of a super conductor is negative which implies that a superconductor exhibits the properties of perfect diamagnetic susbtances.

Isotope effect:

It has been found that the critical temperature (T_C) of superconductor is found to be proportional to the negative half power of isotopic mass of the element i.e.

$$T_C \propto M^{-1/2} \Rightarrow \boxed{M^{1/2}T_C = \text{constant}} \quad \ldots (1)$$

In mercury T_C varies from 4.185 K to 4.146 K, as the isotopic mass (M) varies from 199.5 a.m.u. to 203.4 a.m.u. The debye temperature (θ_D) of phonon spectrum is also proportional to $M^{-1/2}$, so that

$$\theta_D \propto M^{-1/2} \quad \Rightarrow \quad \theta_D M^{1/2} = \text{constant} \quad \ldots (2)$$

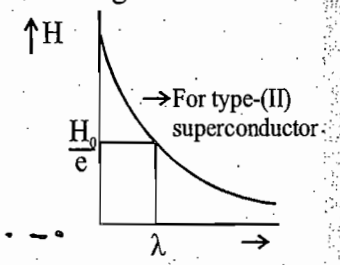
Equation (1) divided by equation (2) gives

$$\boxed{\frac{T_C}{\theta_D} = \text{constant}}$$

Persistent current:

In the super conductors current contineously flows as long as the material is kept below the critical temperature (T_C). Since the current is very high and the decay formula is $i = i_0 e^{-(R/L)t}$. So once started it continue to flow indenfinitely as long as the temperature and magnetic field remain unchanged. This is called the persistent current.

The magnetic field and surface current penetrate in a superconductor to a depth of 10–100 nanaometer.



$$H = H_0 e^{-x/\lambda}$$

Similarly, $J_s = J_0 e^{-x/\lambda}$

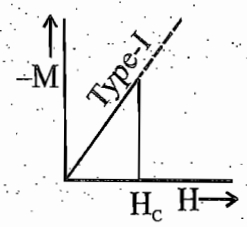
λ = penetration depth

Type-I and type-II superconductors:

Super conductors are classified into the two categories:

(i) Soft (type-I) superconductor, (ii) Hard (type-II) superconductors

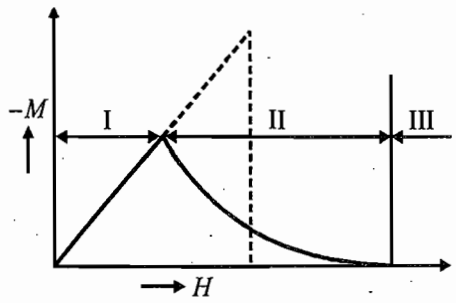
(i) Type-I superconductors: "Superconductor which exhibits complete meissner effect i.e. they are completely diamagnetic are called type-I or soft superconductors". The magnetization curve for type-I superconductor is shown in fig.1. below. It is disappointing that the critical mag. fields of superconductors are very low. Since the super current are started, continuously flow without heat loss. It was thought that magnetic field could be produced and current is maintained without any loss of energy. This is true, but if the magnetic field produced exceed H_C, the material goes normal and current cannot be maintained by it. This was noted in 1916 by Silsbee and is known as Silsbee effect.



(ii) Type-II superconductors:

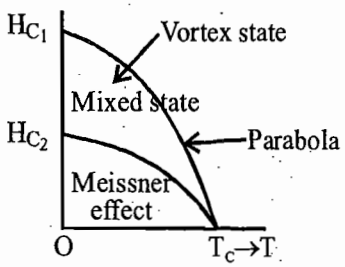
These superconductors behaves differently as shown in Figure. For applied field below H_{C1}, the material is diamagnetism and hence the field is H_{C1} is called the lower critical field. Above H_{C1} magnetic flux begins to enter in the superconductor upto an upper critical field H_{C2} at which superconductivity disappear. The magnetization

curve for type-II superconductor is shown in fig.2a. The magnetic phase diagram for these super conductor is shown in fig.2b.



where, I = Superconducting state
II = Mixed state
III = Normal state

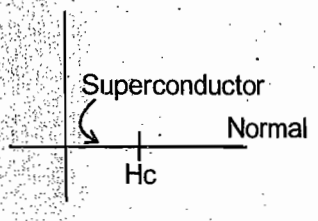
$$H_C = \sqrt{H_{C_1} \times H_{C_2}}$$



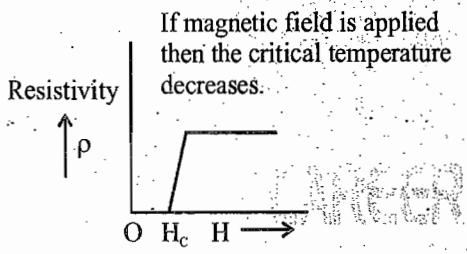
Critical magnetic field:

If a magnetic field is applied parallel to the length of the superconducting wire, the resistance of the wire is suddenly restored at definite magnetic field, which is a function of the temperature and is characteristic of particular metal. This field is known as the critical field magnetic field (H_C). The critical magnetic field H_C is given by the relation

$$H_C = H_{C_0}\left[1-\left(\frac{T}{T_C}\right)^2\right]$$



where H_{C_0} is critical magnetic field at absolute zero.



Penetration depth (λ) :

London described the Meissner effect ($B = 0$) and zero resistivity case of superconductors. He added $E = 0$ for zero resistivity.

As $J = \sigma E$ and $E = \frac{J}{\sigma} = \frac{I}{\infty} = 0$

$B = 0$ according to Meissner effect.

As we know that, $\vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}$

But $\vec{E} = 0 \Rightarrow 0 = \frac{-\partial \vec{B}}{\partial t} \Rightarrow \vec{B} \neq 0$

Then London suggested that applied external magnetic field does not suddenly drop to zero at the surface of superconductor but decays exponentially according to the equation.

$$H = H_0 e^{-x/\lambda}$$

where, H_0 is magnetic field intensity at the surface of the superconductor and λ is characteristic length (known as the penetration depth) at which H falls from H_0 to H_0/e.

London equation:

According to the London theory, it is assumed that there are two types of conduction electrons in a superconductor, namely, the super and the normal electrons. At 0 K a superconductor contains only super electrons but as the temperature increases the number of normal electrons increases and above the transition temperature (T_C) all the electrons are normal.

Let n_n, v_n and n_s, v_s is the electrons density, velocity in normal and superconducting state respectively.

Then the average carrier density $(n) = n_n + n_s$.

The current density $\vec{J} = \vec{J}_n + \vec{J}_s = e\, n_n \vec{v}_n + e n_s \vec{v}_s$ ... (1)

For the superconducting electrons

$$m\frac{d\vec{v}_s}{dt} = e\,\vec{E} \Rightarrow \frac{d\vec{v}_s}{dt} = \frac{e\vec{E}}{m} \qquad \left[\text{as } \vec{F} = m\vec{a} = m\frac{d\vec{v}}{dt} = e\,\vec{E}\right]$$

and $\vec{J}_s = e n_s \vec{V}_s \Rightarrow \quad \frac{d\vec{J}_s}{dt} = e\, n_s \left(\frac{e\vec{E}}{m}\right)$

$$\Rightarrow \quad \boxed{\frac{d\vec{J}_s}{dt} = \frac{n_s\, e^2 \vec{E}}{m}} \qquad \text{... (2)}$$

The equation (2) is known as the first London equation and it describes the absence of resistivity.

If $\vec{E} = 0$

$$\Rightarrow \quad \frac{d\vec{J}_s}{dt} = 0 \quad \Rightarrow \quad \vec{J}_s = \text{constant}$$

Then it becomes possible to have steady (constant) current in the absence of electric field. This is the superconducting phenomenon.

The corresponding equation for the normal current is

$$\boxed{\vec{J}_n = \sigma_n \vec{E} = \frac{n_n e^2 \tau\, \vec{E}}{m}} \qquad \text{... (3)}$$

This equation shows that an electric field is necessary for establishing a steady current in normal metal. If $\vec{E} = 0$, $\vec{J}_n$ becomes zero.

Now by the Maxwell's equation

$$\vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \Rightarrow \vec{\nabla} \times \vec{E} = -\mu_0 \frac{\partial \vec{H}}{\partial t} \qquad \text{... (4)}$$

Now taking curl of equation (2), we get

$$\vec{\nabla} \times \frac{d\vec{J}_s}{dt} = \frac{n_s\, e^2 \left(\vec{\nabla} \times \vec{E}\right)}{m}$$

$$\frac{\partial}{\partial t}\left(\vec{\nabla} \times \vec{J}_s\right) = \frac{n_s e^2}{m}\left(-\mu_0 \frac{\partial \vec{H}}{\partial t}\right) = -\frac{\mu_0 n_s\, e^2}{m}\frac{\partial \vec{H}}{\partial t} \qquad \text{... (5)}$$

Integrating this equation, we get $\boxed{\vec{\nabla}\times\vec{J}_s \equiv -\frac{n_s e^2 \mu_0 \vec{H}}{m}}$ ... (6)

Equation (6) is second London equation and explains meissner effect $\left(i.e.\ \vec{H}=0 \Rightarrow J_s = \text{constant}\right)$.

Calculation of penetration depth (λ):

Taking curl of equation (6) we get

$$\vec{\nabla}\times\left(\vec{\nabla}\times\vec{J}_s\right) = -\frac{n_s e^2 \mu_0}{m}\left(\vec{\nabla}\times\vec{H}\right)$$

Or, $$\vec{\nabla}\left(\vec{\nabla}\cdot\vec{J}_s\right) - \left(\vec{\nabla}\cdot\vec{\nabla}\right)\vec{J}_s = -\frac{n_s e^2 \mu_0}{m}\left(\nabla\times\vec{H}\right) \quad (\text{as } \vec{J}_s = \text{constant})$$

$$\Rightarrow \quad \nabla^2\vec{J}_s = \frac{\mu_0 n_s e^2}{m}\left(\vec{\nabla}\times\vec{H}\right) \qquad \ldots (7)$$

But $$\vec{\nabla}\times\vec{H} = \vec{J} + \frac{\partial\vec{D}}{\partial t} = \vec{J}_n + \vec{J}_s + \frac{\partial\vec{D}}{\partial T}$$

where $\vec{D}$ is the electric displacement vector. For direct current case we can neglect $\vec{J}_n$ and $\frac{\partial\vec{D}}{\partial t}$, so that

$$\vec{\nabla}\times\vec{H} = \vec{J}_s$$

Therefore, equation (7) becomes

$$\nabla^2\vec{J}_s = \frac{\mu_0 n_s e^2}{m}\vec{J}_s = \frac{\vec{J}_s}{\lambda^2} \qquad \ldots (8)$$

where $\boxed{\lambda^2 = \frac{m}{\mu_0 n_s e^2}}$ ... (9)

λ has the dimension of length and is called the penetration depth.

The solution of equation (8) is

$$\boxed{J_s = A\,e^{x/\lambda} + Be^{-x/\lambda}} \qquad \ldots (10)$$

The first factor of this equation shows that J_s increases as x increases which is contrary to the fact. Then it can be left.

Therefore, equation (10) gives $J_s = B\,e^{-x/\lambda}$

at $x = 0,\ J_s = J_0 \Rightarrow B = J_0$

$$\Rightarrow \quad \boxed{J_s = J_0 e^{-x/\lambda}} \qquad \ldots (11)$$

at $x = \lambda,\ J_s = J_0/e$

Thus, λ (penetration depth) is the distance in the superconductor at which the current value falls to $1/e$ of its value at the surface.

Drawback of London theory:

Though the London theory explains the two conditions $E = 0$ and $B = 0$ characterising the superconducting state but it does not tell us about the process happening inside the superconductors. The process which takes place inside the superconductors is explained by BCS theory.

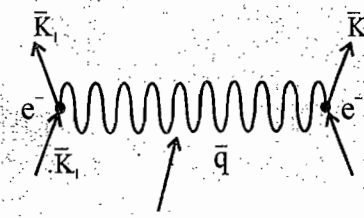
BCS (Bardeen, Cooper and Schrieffer) theory:

This theory explains the microscopic phenomenon which takes place inside the superconductor. It give, the better explanation of the superconductivity than any other theory. This theory involves the following four steps.

(i) Electron-lattice - electron interaction:

When an electron come in contact to the lattice it deforms the lattice and at the same time another electron come in contact to the deformed lattice to take the advantage of lattice deformation. In turns of it the lattice also apply a force on these electrons. Thus, there will be an interaction between electron and electron in which the phonon (lattice vibration) acts as a mediator.

(ii) Cooper pair: The fundamental postulate of BCS theory is that superconductivity phenomenon occurs, when the attractive interaction between two electrons by means of a phonon exchange dominates the usual repulsive coulomb interaction. Two such electrons which interact attractively in the phonon field are called a Cooper pair. These Cooper pairs behave like a single particle. The energy of the pair of electrons in the ground state is less than the energy of the pair in free state (electron separated). The difference of the energy of the Cooper pair and that of the energy of the Cooper pair and that of free electrons is equal to the binding energy of the Cooper pair. At temperature less than T_C electron-lattice-electron interaction is stronger than electron-electron Coulomb repulsion. Pairing is complete at $T = 0$ K and is completely broken at $T = T_C$.



Electron–electron interaction through lattice phonon

(iii) Existance of Energy gap:

The energy difference between the free state of electrons and the paired state appears as the energy gap at the Fermi surface. The gap is maximum at absolute zero temperature and becomes zero at $T = T_C$

(iv) The paired electrons (Cooper pair) are not scattered because of their special property of smooth riding over the lattice imperfection without exchanging of energy with them. As a result of this they travel a certain distance in the coupled motion. This distance is called coherence length. It is of the order of 10^{-4} cm. Coherence length $(\xi_o) = \dfrac{\hbar v_F}{\pi E_g}$; where, v_F = Velocity at Fermi-surface.

Expression for coherence length:

The London penetration depth (λ_L) is a fundamental length that characterises a superconductor. Another independent length of equal importance is the coherence length (ξ_0).

Now the modulated wavefunction corresponding to wave function

$$\psi = e^{+ikx} \text{ is } \phi = \frac{1}{\sqrt{2}}\left[e^{i(k+q)x} + e^{ikx}\right] \qquad ..(1)$$

Now the probability density corresponding to ϕ is

$$\phi^*\phi = \frac{1}{\sqrt{2}}\left[e^{-i(k-q)x} + e^{-ikx}\right].\frac{1}{\sqrt{2}}\left[e^{i(k-q)x} + e^{ikx}\right]$$

$$= \frac{1}{2}\left[1+1+e^{-iqx}+e^{iqx}\right] = \frac{1}{2}\left[2+2\cos qx\right]$$

$$\Rightarrow \quad \phi^*\phi = \left[1+\cos qx\right] \qquad \ldots (2)$$

The probability associated with the plane wave is

$$\psi^*\psi = e^{-ikx}\cdot e^{-ikx} = 1$$

The kinetic energy (E) of the wave function $\psi(x) = \frac{\hbar^2 k^2}{2m}$ ... (3)

While the K.E. for the modulated wave function ϕ is

$$\int\phi\left(\frac{\hat{p}^2}{2m}\right)\phi\,dx = \int\phi^*\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\phi\,dx = \int\left[\frac{1}{\sqrt{2}}\left(e^{-i(k+q)x}+e^{-ikx}\right)\right]\left(\frac{-\hbar^2}{2m}\right)\frac{d^2}{dx^2}\left[\frac{1}{\sqrt{2}}\left(e^{i(k+q)x}+e^{ikx}\right)\right]dx$$

$$= +\frac{\hbar^2}{4m}\int\left[e^{-i(k+q)x}+e^{-ikx}\right]\left[(k+q)^2+k^2\right]\left[e^{i(k+q)x}+e^{ikx}\right]dx$$

$$= \frac{\hbar^2}{4m}\left[(k+q)^2+k^2\right]\int\left[e^{-i(k+q)x}+e^{-ikx}\right].\left[e^{i(k+q)x}+e^{ikx}\right]dx$$

$$= \frac{\hbar^2}{4m}\left[2k^2+2kq+q^2\right] \simeq \frac{\hbar^2}{2m}k^2 + \frac{\hbar^2}{2m}kq \qquad (\text{As } q << k)$$

Thus the increase in energy $= \frac{\hbar^2 kq}{2m}$ ... (4)

If this increase in energy exceeds the energy gap E_g, the superconductivity will be destroyed. The critical value of q_0 of the modulation vector is given by

$$\frac{\hbar^2 k_F q_0}{2m} = E_g \qquad \ldots (5)$$

The intrinsic length (ξ_0) is defined as

$$\xi_0 = \frac{1}{q_0} = \frac{\hbar^2 k_F}{2mE_g} = \frac{\hbar P_F}{2mE_g} \Rightarrow \boxed{\xi_0 = \frac{\hbar v_F}{2E_g}}$$

By BCS theory, $\boxed{\xi_0 = \frac{\hbar v_F}{\pi E_g}}$

$\frac{\lambda}{\xi_0} = k$ and $k > \frac{1}{\sqrt{2}}$, for type-I superconductors and $k < \frac{1}{\sqrt{2}}$, for type-II superconductors.

Properties which change in the superconducting transitions:

(i) All the thermoelectric effects disappear in the superconducting state.

(ii) The specific heat changes discontinuously at the transition temperature in the pressure of magnetic field.

(iii) There is also a small change in volume, in presence of magnetic field.

(iv) The thermal conductivity changes discontinuously when superconductivity is destroyed in a magnetic field.

Properties which do not change in superconducting transitions:

(i) There is no change in the reflectivity (reflection coefficient) of the metal.

(ii) The X-ray diffraction pattern is same.

(iii) The photoelectric properties, remain unchanged.

(iv) The elastic properties do not change.

(v) In the atom of a magnetic field there is no latent heat and hence no change in volume at the transition.

Superconducting band gap: $E_g = 3.53\, k_B T_C \simeq 4 k_B T_C$

Cooper pair follow Bose-Einstein statistics. Its spin is zero.

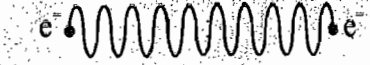
Superconductivity is of II[nd] order phase transition.

Main points of BCS theory of superconductivity:

The basis of a quantum theory of superconductivity was laid by the classic 1957 papers of Bardeen, Cooper and Schrieffer. The BCS theory include:

(i) An attractive interaction between electrons can lead to a ground state seperated from excited state by an energy gap. The critical field, the thermal properties and the most of the electromagnetic properties are consequencies of the energy gap.

(ii) The electron-lattice-electron interaction leads to an energy gap of the observed magnitude. The indirect interaction proceeds when one electron interacts with the lattice and deforms it; a second electron sees the deformed lattice and adjusts itself to take advantage of the deformation to lower its energy. Thus the second electron interacts with the first electron via the lattice deformation.



(iii) The penetration depth of coherence length emerge as natural consequences of the BCS theory.

(iv) The criterion for the transition temperature T_C of an element or alloy involves the electron density of orbitals $D(E_F)$ at the Fermi level and the attractive electron-lattice-electron interaction (U) and is given by

$$T_C = 1.14\,\theta_D \exp\left[-1/UD(E_F)\right]$$

(v) Magnetic flux through the superconducting ring is quantized and the effective unit of charge is 2e rather than e. $\phi = n\dfrac{h}{2e}, n = 1, 2, 3.....$ The BCS ground state involves pairs of electrons, having opposite wave vectors of opposite spins: $\vec{k}_1 = -\vec{k}_2$ and $s_1 = -s_2$. Such pairs of electrons are called as the Cooper pairs.

THERMODYNAMICS OF SUPERCONDUCTORS:

(i) Entropy in normal state : $S_n = S_s - \mu_0\left[H_C \dfrac{dH_C}{dT}\right]$, where S_n is entropy of normal state and S_s is entropy of superconducting state.

At $T = T_C' \Rightarrow H_C = 0 \quad \Rightarrow \Delta S = S_n - S_s' = 0$

Thus, $S_n = S_s$ i.e. entropy is continuous at the transition point (T_C).

(ii) Change in specific heat at T_C:

$$\Delta C = C_s - C_n = \mu_0 T_C \left(\frac{dH_C}{dT}\right)^2$$, this is known as Rutger formula.

At $T = T_C$, $\Delta C \neq 0$

Therefore, specific heat is discontinuous at the transition point (T_C).

JOSEPHSON SUPERCONDUCTOR TUNNELING:

There are many effects associated with the tunelling of superconducting electron-pairs from a superconductor through a layer of an insulator into another superconductor. Such a junction is called a weak link. Few of such effects are:

(1) DC Josephson effect: A dc current flows across the junction in the absence of any electric and magnetic field.

(2) AC Josephson effect: A dc voltage applied across the junction causes radio frequency current oscillations across the junction. This effect is utilized for precise measurement of $\hbar/e$. Further a radio frequency voltage applied with dc voltage can then cause an ac current of frequency $\omega = \frac{2eV}{\hbar}$.

CAREER ENDEAVOUR

SOLVED PROBLEMS

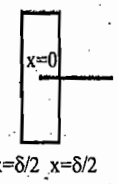
1. A superconducting tin has a critical temperature of 3.7 K in zero magnetic field and a critical field of 0.0306 T at 0 K. Find the critical field at 2 K,

Soln. $H_C = H_{C_0}\left[1-\left(\frac{T}{T_C}\right)^2\right] \Rightarrow H_C = 0.0306\left[1-\left(\frac{2}{3.7}\right)^2\right] = 0.0231\,\text{T}$

2. The penetration equation may be written as $\lambda^2\nabla^2 B = B$, where λ is the penetration depth. Show that $B(x)$ inside a superconducting plate perpendicular to the x-axis and of thickness δ is given by $B(x) = B_a \frac{\cosh {}^{x}/_{\lambda}}{\cos h\left({}^{\delta}/_{2\lambda}\right)}$

Where B_a is the field outside the plate and parallel to it, and $x = 0$ is at the plate.

Soln. $\nabla^2 B = \frac{B}{\lambda^2}$



$\Rightarrow \quad B = Ae^{{}^{x}/_{\lambda}} + A'e^{-{}^{x}/_{\lambda}}$ ... (1)

Applying the condition

$B = B_a$ at $x = {}^{\delta}/_{2}$ and $x = -{}^{\delta}/_{2}$

$\Rightarrow \quad B_a = Ae^{{}^{\delta}/_{2\lambda}} + A'e^{-{}^{\delta}/_{2\lambda}}$

Also, $B_a = Ae^{-{}^{\delta}/_{2\lambda}} + A'e^{{}^{\delta}/_{2\lambda}} \quad \Rightarrow \quad A = A'$ ... (2)

$\therefore \quad B_a = A\left(e^{{}^{\delta}/_{2\lambda}} + e^{-{}^{\delta}/_{2\lambda}}\right) = A\left(2\cosh {}^{\delta}/_{2\lambda}\right)$

$\Rightarrow \quad A = {}^{B_a}/_{2\cosh\left({}^{\delta}/_{2\lambda}\right)}$ ... (3)

Putting equation (2) and equation (3) in equation (1), we get

$$B = B_a\left(\frac{\cosh {}^{x}/_{\lambda}}{\cosh {}^{\delta}/_{2\lambda}}\right)$$

3. If $H_C = H_{C_0}\left[1-\frac{T^2}{T_C{}^2}\right]$ and $C_n = rT_C$, show that fractional charge in the heat capacity at the discontinuity is given by, $\frac{C_s - C_n}{C_n} = \frac{4\mu_0 H_{C0}^2}{rT_C^2}$.

Soln. $C_s - C_n = \mu_0 T_C\left(\frac{dH_C}{dT}\right)^2$ ... (1)

and $H_C = H_{Co}\left[1-\frac{T^2}{T_C^2}\right] \quad \Rightarrow \quad \frac{dH_C}{dT} = H_{Co}\left(0-\frac{2T}{T_C^2}\right)$

$\Rightarrow \quad \left(\frac{dH_C}{dT}\right)^2 = 4\frac{H_{Co}^2 T^2}{T_C^4}$ ... (2)

Putting equation (2) in equation (1), we get

$$C_s - C_n = \frac{4\mu_0 H_{Co}^2 T^2}{T_C^3}$$

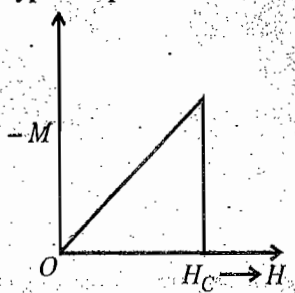
$$\therefore \quad \frac{C_s - C_n}{C_n} = \frac{C_s - C_n}{rT_c} = \frac{4\mu_0 H_{Co}^2 T^2}{rT_C^4}$$

At discontinuity $T = T_C$; $\frac{C_s - C_n}{C_n} = \frac{4\mu_0 H_{Co}^2 T_C^2}{rT_C^4}$

$$\Rightarrow \quad \boxed{\frac{C_s - C_n}{C_n} = \frac{4\mu_0 H_{Co}^2}{rT_C^2}}$$

4. An external magnetic field of magnitude H is applied to a type-I superconductor at temperature below the transition point. Then which one of the following statements is not true for H less than the critical field H_C?
(a) The sample is diamagnetic. **[GATE 2003]**
(b) Its magnetization varies linearly with H.
(c) The lines of magnetic induction are pushed out from the sample.
(d) The sample exhibits mixed states of magnetization near H_C.

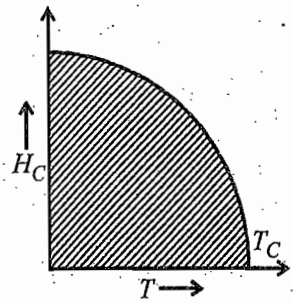
Soln. Below H_C, the sample behaves as a diamagnetic. Its magnetization varies linearly with H (slope $= -1$) and Meissner effect will be followed by the superconductor. The statement "the sample exhibits mixed states of magnetization near H_C" is not true for type-I superconductor. It is true for type-II superconductors.



Hence, correct option is (d).

5. The critical magnetic field for a solid in superconducting state **[GATE 2004]**
(a) does not depend upon temperature
(b) increases if the temperature increases
(c) increases if the temperature decreases
(d) does not depend on the transition temperature

Soln. $\because \quad H_C(T) = H_C(0)\left[1 - \frac{T^2}{T_C^2}\right]$, where $H_C(0)$ is critical field at 0 K. Now, if T increases, T^2 will also increase.



Thus, $H_C(T)$ will decrease.
Hence, correct option is (c).

6. For a conventional superconductor, which of the following statements is not correct (true) ?

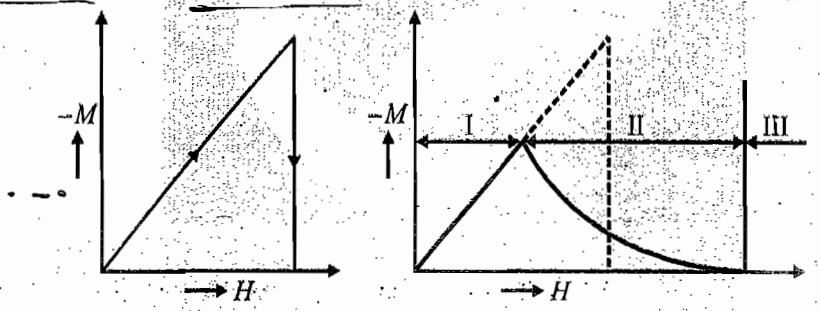
(a) specific heat is discontinuous at certain transition temperature T_C **[GATE 2005]**
(b) The resistivity falls sharpely at T_C
(c) It is diamagnetic below T_C
(d) It is paramagnetic below T_C

Soln. The statement "It is paramagnetic below T_C" is not correct as $B = 0 \Rightarrow \mu_0 (H + M) = 0 \Rightarrow H = -M$
$\Rightarrow \chi = -1$, which implies that superconductor is diamagnetic below T_C.
Hence, correct option is (d).

7. Which one of the following statements about superconductors is not true ? **[GATE 2006]**

(a) A type-I superconductor is completely diamagnetic.
(b) A type-II superconductor exhibits Meissner effect upto the second critical magnetic field (H_{C_2}).
(c) A type-II superconductor exhibits zero resistance upto the second critical magnetic field (H_{C_2}).
(d) Both type-I and type-II superconductor exhibit sharp fall in resistance at the superconducting transition temperature.

Soln. Type-I superconductors exhibit complete Meissner effect and are completely diamagnetic. Type-II superconductors exhibit complete Meissner effect upto H_{C_1} only. Above H_{C_1}, the flux begins to penetrate the speciman and for $H = H_{C_2}$, the complete penetration occurs and material becomes completely normal conductor. In the region between the field H_{C_1} and H_{C_2}, the Meissner effect is not strictly followed.

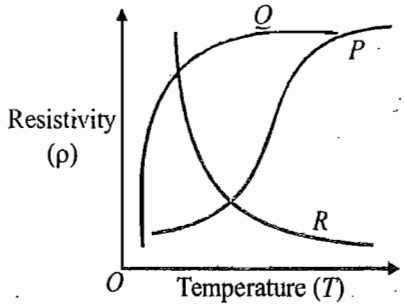


Type-I superconductor **Type-II superconductors**

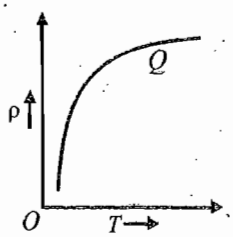
Therefore, the statement in option (b) is not true.
Hence, correct option is (b).

8. Variation of electrical resistivity ρ with temperature T of three solids is sketched (on different scales) in the figure, as curves P, Q and R. Which one of the following statements describes the variation most appropriately?

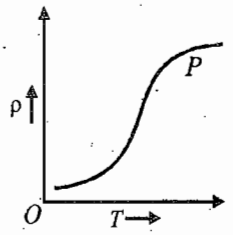
(a) P is for a superconductor, and R for a semiconductor. **[GATE 2007]**
(b) Q is for a superconductor, and P for a conductor.
(c) Q is for a superconductor, and R for a conductor.
(d) R is for a superconductor, and P for a conductor.



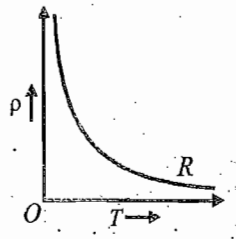
Soln. For superconductors, $\rho - T$ graph is



For conductors, $\rho - T$ graph is



For semiconductors, $\rho - T$ graph is



Hence, correct option is (b).

9. A solid superconductor is placed in an external magnetic field and then cooled below its critical temperature. The superconductor **[GATE 2007]**

(a) retains its magnetic flux because the surface current supports it
(b) expels out its magnetic flux because it behaves like a paramagnetic material
(c) expels out its magnetic flux because it behaves like an antiferromagnetic material
(d) expels out its magnetic flux because the surface current induces a field in the direction opposite to the applied magnetic field

Soln. According to Meissner effect, the superconductor expels out its magnetic flux because the surface current induces a field in the direction opposite to the applied magnetic field.
Hence, correct option is (d).

10. A superconducting ring is cold in the presence of a magnetic field below its critical temperature (T_C). The total magnetic flux that passes through the ring is **[GATE 2009]**

(a) zero (b) $\frac{nh}{2e}$ (c) $\frac{nh}{4\pi e}$ (d) $\frac{ne^2}{hc}$

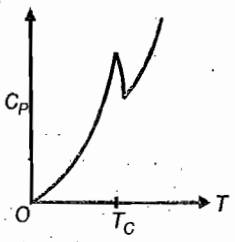
Soln. According to Meissner effect, the total magnetic flux that passes through the ring is zero.
Hence, correct option is (a).

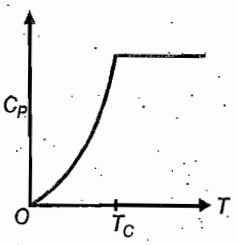
11. Considering the BCS theory of superconductors, which one of the following statements is not correct ? (h is Planck's constant and e is the electronic charge) **[GATE 2013]**

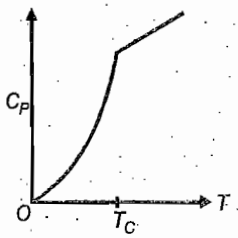
(a) presence of energy gap at temperatures below the critical temperature.
(b) different critical temperature for isotopes.
(c) quantization of magnetic flux in superconducting ring in the unit of (h/e).
(d) presence of Meissner effect.

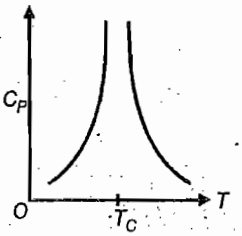
Soln. Considering the BCS theory of superconductors the statement "(c) Quantization of magnetic flux in superconducting ring in the unit of (h/e)" is not correct. It correctly predicts the Meissner effect, isotope effect and band gap in the superconductor.
Hence, correct option is (c).

12. The plot of specfic heat versus temperature across the superconductor transition temperature (T_C) is most appropriately represented by **[GATE 2014**

(a) 

(b) 

(c) 

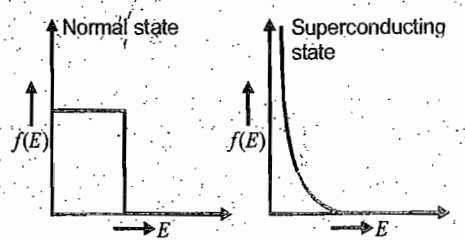
(d) 

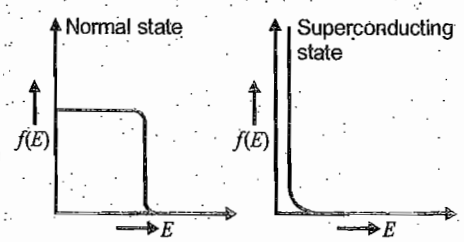
Soln. The specific heat. $C = C_{\text{él.}} + C_{\text{lattice}}$

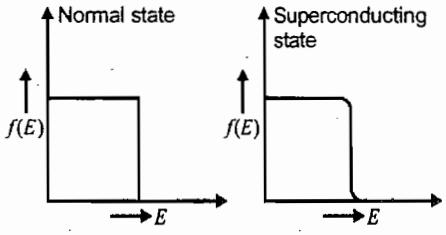
Since, $(C_{\text{el.}})_{\text{superconductor}} = a \exp\left(-\frac{\Delta}{k_B T}\right)$, where a is a constant and Δ is energy gap.

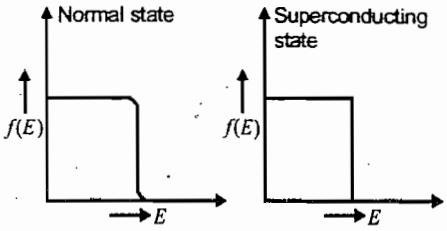
i.e., the specific heat of a superconductor shows discontinuous at transition temperature.
Therefore, the electronic specific heat of a metal in the superconducting state varies with temperature in an exponential manner.
Hence, correct option is (a).

13. Which one of the following represents the electron occupancy for a superconductor in its normal and superconducting states ? **[GATE 2015]**

(a) 

(b) 

(c) 

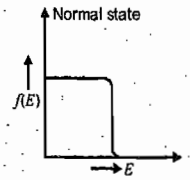
(d) 

Soln. The superconductor behaves like a normal conductor above transition temperature (T_C) and below T_C, it exhibits superconductivity.

In normal state the electrons will have $\frac{1}{2}$-integral spin and will follow Fermi-Dirac distribution function

$$f(E)=\frac{1}{\left(e^{(E-E_F)/k_BT}+1\right)}$$

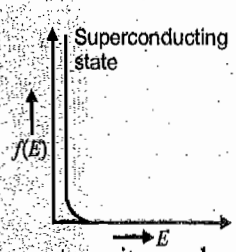
Therefore, $f(E)$ versus E graph $(T>0\,\text{K})$ will be



In superconducting state, electrons form cooper pairs with spin = 0.
Hence these electrons in superconducting state will follow Bose-Einstein distribution function.

$$f(E)=\frac{1}{\left(e^{(E-E_F)/k_BT}-1\right)}$$

Therefore, $f(E)$ versus E graph $(T>0\,\text{K})$ will be



Hence, correct option is (b).

14. A solid sample has the property that, when cooled below a certain temperature, it expels any small applied magnetic field form within the material. Which of the following best describes this sample in the cooled state ?

(a) Paramagnet (b) Diamagnet (c) Ferromagnet (d) Antiferromagnet

[TIFR-2014]

Soln. The sample expels the applied magnet field from within the material. In cooled state, it shows superconductivity.

i.e., $B_{in}=0$

$\Rightarrow \mu_0(H+M)=0$

$\Rightarrow H=-M$

$\Rightarrow \chi=-\frac{M}{H}=-1$

i.e., magnetic susceptibility (χ) is unity with negative sign.
Hence, the sample will be a diamagnetic.
Hence, correct option is (b).

PRACTICE SET

1. Lead in the superconducting state has the critical temperature of 6.2 K at zero magnetic field and a critical field of 0.064 MAm^{-1} at 0 K. Determine the critical field at 4 K.
2. The transition temperature of mercury with an average atomic mass of 200.59 amu is 4.153 K. Determine the transition temperature of one of its isotopes, $_{80}Hg^{204}$.
3. The critical temperature of a superconductor at zero magnetic field is T_C. Determine the temperature at which the critical field becomes half of its value at 0 K.
4. The critical fields at 6 K and 8 K for a NbTi alloy are 7.616 and 4.284 MAm^{-1} respectively. Determine the transition temperature and the critical field at 0 K.
5. Determine the frequency of the electromagnetic waves radiated by a Josephson junction across which a dc voltage of 0.5 mV is applied.
6. Calculate the critical current which can flow through a long thin superconducting wire of a aluminium of diameter 10^{-3} m. The critical field for aluminium is 7.9×10^3 A/m
7. A superconducting lead has a critical temperature of 7.26K at zero magnetic field and a critical field of 8×10^5 A/m at 0K. Find the critical field at 5 K
8. The critical current flowing through a long thin superconducting wire of aluminium of diameter 10^{-4}m, the corresponding critical field is

   (a) 7.9×10^3 A/m (b) 7.9×10^4 A/m (c) 7.9×10^5 A/m (d) 7.9×10^6 A/m
9. The penetration depths for lead are 396Å and 1730 Å at 3 K and 7.1 K, respectively. The critical temperature for lead is

   (a) 4.193 K (b) 5.193 K (c) 6.193 K (d) 7.193 K
10. A DC voltage of 5 μV is applied across the Josephson junction, the frequency of the AC current produced is

    (a) 2.41×10^8 *Hz* (b) 2.41×10^9 *Hz* (c) 2.41×10^{10} *Hz* (d) 2.41×10^{11} *Hz*

ANSWER KEY

1. (0.037 MAm^{-1}) **2. (4.118K)** **3. (0.707 T_c)** **4. (10K, 11.9 MAm^{-1})**
5. (2.41×10^{11} Hz) **6. (24.81 Å)** **7. (4.2×10^5 A/m)** **8. (a)**
9. (d) **10. (b)**

Chapter 12

DEFECTS IN CRYSTALS

In this chapter, we will discuss different types of imperfections or defects in the ideal arrangement of atoms in a crystal. We will see that the presence of a relatively small number of defects have a profound impact on the macroscopic properties of materials, and the control (and intentional introduction) of defects is important in many kinds of material processing.

Examples of the relevance of defects in crystals for life in general or materials science in particular: When/if you buy a diamond ring, it is mostly the number and type of defects in the diamond crystal that define the amount of money you pay for a given crystal size. It is generation, accumulation, and interaction of defects in different parts of your car that define the mileage on your car when you tow it to the junk-yard. Production of advanced semiconductor devices requires not only a rather perfect Si crystal as starting material, but also involve introduction of specific defects in small areas of the sample. Forging a metal tool introduces defects and increases strength and elasticity of the tool. Note, that in this case the required properties are achieved without changes in composition of the material, but just by manipulating the crystal defects.

The three basic classes of defects in crystals:

Point defects (zero dimensional): atoms missing or in irregular places in the lattice (lattice vacancies, substitutional and interstitial impurities, self-interstitials).

Line defects (one dimensional): groups of atoms in irregular positions (e.g. screw and edge dislocations).

Planar defects (two dimensional): the interfaces between homogeneous regions of the material (grain boundaries, stacking faults, external surfaces).

CAREER ENDEAVOUR

Point Defects:

(1) Vacancies:

A perfect crystal with regular arrangement of atoms cannot exist. There are always defects, and the most common defects are point defects. This is especially true at high temperatures when atoms are frequently and randomly change their positions leaving behind empty lattice sites, called **vacancies.** In most cases diffusion (mass transport by atomic motion) - can only occur because of vacancies.

How many vacancies are there? The higher is the temperature, more often atoms are jumping from one equilibrium position to another and larger number of vacancies can be found in a crystal. Actually, the number of vacancies, N_v, increases exponentially with the absolute temperature, T, and can be estimated using the equation (Boltzmann distribution):

$$N_v = N_s \exp\left(-\frac{E_v}{k_B T}\right)$$

where N_s is the number of regular lattice sites, k_B is the Boltzmann constant, and E_v is the energy needed to form a vacant lattice site in a perfect crystal. Using this simple equation we can estimate that at room temperature in copper there is one vacancy pet 10^{15} lattice atoms, whereas at high temperature, just below the melting point there is one vacancy for every 10,000 atoms. These are the lower end estimations, a large numbers of additional vacancies can be introduced in a growth process or as a result of further treatment (plastic deformation, quenching from high temperature to the ambient one, etc.).

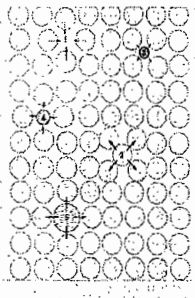
(2) Interstitials:

Atoms that are squeezed in between regular lattice sites are called interstitial atoms. If the interstitial atom is of the same species as the lattice atoms, it is called self-interstitial. Creation of a self-interstitial causes a substantial distortions in the surrounding lattice and costs more energy as compared to the energy for creation of a vacancy ($E_i > E_v$) and, under equilibrium conditions, self-interstitials are present in lower concentrations than vacancies. Foreign, usually smaller atoms (carbon, nitrogen, hydrogen, oxygen) are called interstitial impurities. They introduce less distortion to the lattice and are more common in real materials and more mobile. If the foreign atom atom replaces or substitutes for a matrix atom, it is called a substitutional impurity.

As shown in the schematic drawing, all point defects introduce local distortions to the lattice, and due to these distortions they can feel each other (interact) and feel external stresses. The external stresses or stresses from a larger defects that we will consider next can give a directionality to an otherwise random jumps of atoms. In particular, a pressure gradient results in a flux of vacancies in the direction towards a compressed region of the sample.

For equilibrium minimum Gibbs free energy G at constant T and P.

A certain concentration of vacancy lowers the free energy of a crystal.



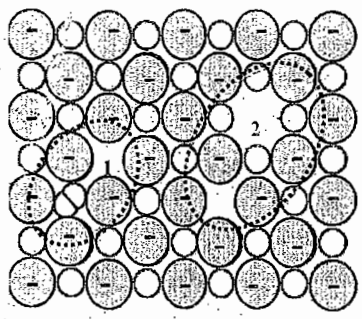
Schematic representation of different point defects in a crystal. (1) Vacancy; (2) selfinterstitial; (3) interstitial impurity; (4), (5) substitutional impurities. The arrows show the local stresses introduced by the point defects.

In ionic crystals (e.g. table salt – Na^+Cl^-) the bonding is provided by coulombic forces between positively and negatively charged ions. Point defects in ionic crystals are charged as well. The Coulombic forces are very large and any charge imbalance has a very strong tendency to balance itself. To maintain charge neutrality several point defects can be created.

Frenkel defect: A Frenkel defect is a pair of cation (positive ion) vacancy and a cation interstitial, or it may also be an anion (negative ion) vacancy and anion interstitial. However anions are much larger than cations and it is not easy for an anion interstitial to form.

Schottky defect: A Schottky defect is a pair of anion and cation vacancies.

In both Frenkel and Schottky defects, the pair of point defects stays near each other because of strong coulombic attraction of their opposite charges.



Schematic representation of (1) Frenkel defect (vacancy-interstitial pair) and (2) Schottky defect (a pair of cation and anion vacancies) in an ionic crystal.

Line defects: dislocation in metals :

(1) Edge Dislocation: A portion of an extra plane of atoms.
(2) Screw Dislocation: Helical atomic displacement around a line extending through the crystal.
(3) Mixed Dislocation: Some edge, some screw nature.

The interatomic bonds are significantly distorted only in the immediate vicinity of the dislocation line. This area is called the **dislocation core**. Dislocations also create small elastic deformations of the lattice at large distances. To describe the size and the direction of the main lattice distortion caused by a dislocation we should introduce so-called **Burgers vector** $\boldsymbol{b}$. To find the Burgers vector, we should make a circuit from from atom to atom counting the same number of atomic distances in all directions. If the circuit encloses a dislocation it will not close. The vector that closes the loop is the Burgers vector $\boldsymbol{b}$. Dislocations that have been considered until now have Burgers vector directed perpendicular to the dislocation line. These dislocations are called **edge dislocations**. There is a second basic type of dislocation, called **screw dislocation**. The screw dislocation is parallel to direction in which the crystal is being displaced (Burgers vector is parallel to the dislocation line). In general, there can be any angle between the Burgers vector $\boldsymbol{b}$ (magnitude and the direction of slip) and the line vector $\boldsymbol{t}$ (unit vector tangent to the dislocation line).

$\boldsymbol{b} \perp \boldsymbol{t}$ $\Rightarrow$ Edge dislocation

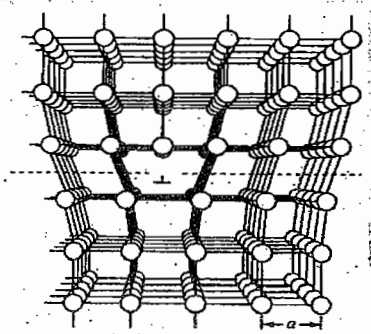
$\boldsymbol{b} \parallel \boldsymbol{t}$ $\Rightarrow$ Screw dislocation

$\boldsymbol{b} \perp \boldsymbol{t}, \boldsymbol{b} \parallel \boldsymbol{t}$ $\Rightarrow$ Mixed dislocation

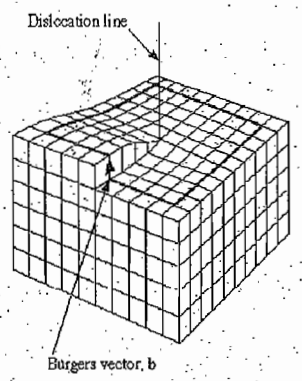
Line energy of a dislocation:

Elastic energy per unit length of a dislocation line $E = \frac{1}{2}\mu b^2$ Unit: J m^{-1}

where, μ is shear modulus of the crystal and b is length of the Burgers vector.

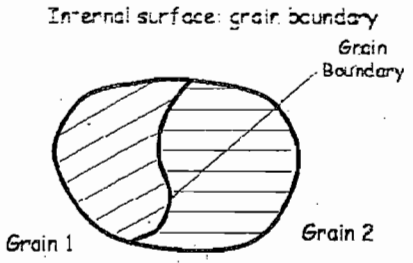


Edge dislocation



Screw dislocation

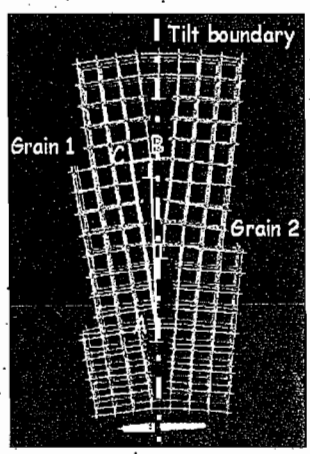
Planar defects: Grain Boundaries:



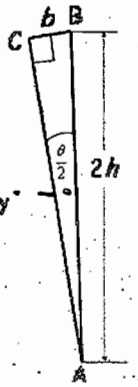
A grain boundary is a boundary between two regions of identical crystal structure but different orientation

Grain Boundary: tilt and twist. One grain orientation can be obtained by rotation of another grain across the grain boundary about an axis through an angle. If the axis of rotation is perpendicular to the boundary plane it is called a twist boundary.

Grain Boundary: low and high angle. One grain orientation can be obtained by rotation of another grain across the grain boundary about an axis through an angle. If the angle of rotation is high, it is called a high angle grain boundary. If the angle of rotation is low it is called a low angle grain boundary.



Edge dislocation model of a small angle tilt boundary



$$\frac{b}{2h} = \sin\frac{\theta}{2}$$

Or approximately

$$\frac{b}{h} = \tan\theta$$

Eqn. 6.7

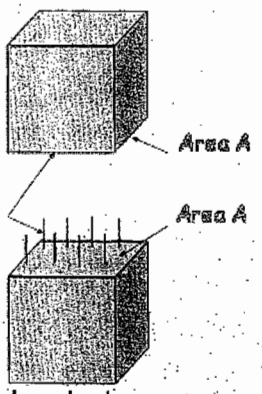
External surface: Free surface

n_A = Number of surface per unit area

n_B = Number of broken bands per surface atom

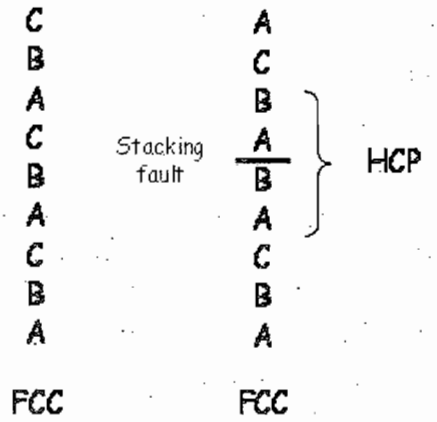
ε = Bond energy per atom

Surface energy per unit area $\gamma = \frac{1}{2} n_A n_B \varepsilon$



If bond are broken over an area A then two free surfaces of a total area 2A is created

Stacking fault



Color centers:

Pure alkali halide crystals are transparent to visible region of spectrum. A color centre is a lattice defect that absorb visible light. Electrons trapped in vacant sites give rise to colour centers.

Trapped electrons can be produced by

(i) Irradiation of the sample (ii) Treatment with an electron donor like sodium or potassium vapour.

***F*, *H* and *V* centers**

Irradiation can lead to defects where can an electron has been lost or added.

Treatment with alkali metal vapor can lead to excess electrons in material.

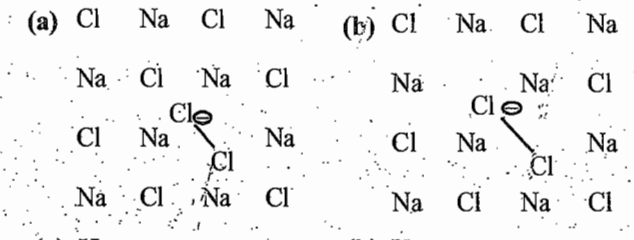
***F*- centre:** Electron trapped in anion vacancy

Example of color center as trapped electron lead to absorption in visible.

Cl	Na	Cl	Na	Cl
Na	Cl	Na	Cl	Na
Cl	Na	e	Na	Cl
Na	Cl	Na	Cl	Na
Cl	Na	Cl	Na	Cl

***H*-centre :** intertitial Cl atom bonds to lattice Cl^-.

***V*-centre :** electron removed from lattice anion site, resulting Cl atom pairs with neighbouring Cl^- in NaCl.



(a) *H*-centre (b) *V*-centre

***M*-centre** consist of two adjacent *F*-centres.

***R*-centre** consist of three adjacent *F*-centres that mean it is a group of three negative ion vacancies.

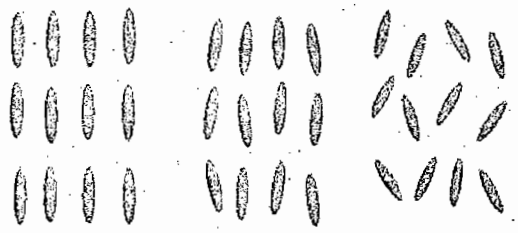
Note:

Mechanism of electrical conductivity in alkali and silver halide crystals is usually the motion of ions and not the motion of electrons. This has been established by comparing the transport of charge with the transport of mass as measured by the material plated out on electrodes in contact with the crystal.

What are Liquid crystals?

Liquid crystal materials generally have several common characteristics. Among these is a rod-like molecular structure, rigidness of the long axis, and strong dipoles and/or easily polarizable substituents.

The distinguishing characteristic of the liquid crystalline state is the tendency of the molecules (mesogens) to point along a common axis, called the director. This is in contrast to molecules in the liquid phase, which have no intrinsic order. In the solid state, molecules are highly ordered and have little translational freedom. The characteristic orientational order of the liquid crystal state is between the traditional solid and liquid phases and this is the origin of the term mesogenic state, used synonymously with liquid crystal state. Note the average alignment of the molecules for each phase in the following diagram.



Solid **Liquid Crystal** **Liquid**

It is sometimes difficult to determine whether a material is in a crystal or liquid crystal state. Crystalline materials demonstrate long range periodic order in three dimensions. By definition, an isotropic liquid has no orientational order. Substances that aren't as ordered as a solid, yet have some degree of alignment are properly called liquid crystals.

Liquid crystals can distinguish from isotropic liquid and perfect crystal by an order parameter (S). In an isotropic liquid, order parameter is equal to zero. For a perfect crystal, the order parameter evaluates to one. Typical values for the order parameter of a liquid crystal range between 0.3 and 0.9, with the exact value a function of temperature, as a result of kinetic molecular motion. The tendency of the liquid crystal molecules to point along the director leads to a condition known as anisotropy. This term means that the properties of a material depend on the direction in which they are measured.

Characterizing liquid crystals:

The following parameters describe the liquid crystalline structure:

(1) Positional order

(2) Orientational order

(3) Bond orientational order

Positional order:
The extent to which the position of an average molecule or group of molecules shows translational symmetry.

Orientation order:
Measure of the tendency of the molecules to align along the director on a long-range basis. See order parameter.

Bond orientational order:
Describes a line joining the centers of nearest-neighbor molecules without requiring a regular spacing along that line. Thus, a relatively long-range order with respect to the line of centers but only short range positional order along that line.

SOLVED PROBLEMS

1. The energy of formation of a vacancy in copper is 1 eV. Estimate the relative change in the density of copper due to vacancy formation at a temperature just below its melting point, 1356 K.

Soln. Using the same equation as above, we find

$$\frac{n}{N}=\exp\left(-\frac{E}{k_BT}\right)=\exp\left(-\frac{1}{8.614\times10^{-5}\times1356}\right)=\exp(-8.56)=1.914\times10^{-4}$$

Therefore, the number of vacancy per mole is

$$n=6.023\times10^{23}\times1.914\times10^{-4}=1.1528\times10^{20}$$

Now, the change in the density due to creation of vacancy is

$$n+N=6.0241528\times10^{23}$$

Therefore, the relative change in the density of copper due to vacancy formation is

$$\frac{n+N}{N}=1.0001914:1$$

2. The energy required to remove a pair of ions, Na^+ and Cl^-, from NaCl is ~2 eV. Calculate the approximate number os Schottky imperfections present in the NaCl crystal at room temperature.

Soln. Given: Temperature $T=300$ K and energy required to remove a pair of ions = 2 eV

Therefore, using the expression

$$\frac{n}{N}=\exp\left(-\frac{E}{2k_BT}\right)=\exp\left(-\frac{2}{2\times8.61\times10^{-5}\times300}\right)$$

$$=\exp(-38.70)=1.564\times10^{-17}$$

Or, $n=6.023\times10^{23}\times1.564\times10^{-17}=9.42\times10^{6}$

Now, since the volume of one mole of the crystal = 26.83 cm^3,

Therefore, $n=\frac{9.42}{26.83}\times10^{6}=0.35\times10^{6}\ cm^{-3}$

PRACTICE SET

1. Determine the fraction of atoms in a given solid with the energy equal to or greater than 1.5 eV at room temperature (300 K) and at 1500 K.
2. The concentration of Schottky defects in an fcc crystal is 1 in 10^{10} at a temperature of 300 K. Estimate the average separation between the defects in terms of lattice spacing at 33 K and calculate the value of concentration to be expected at 1000 K.
3. The energy required to remove a pair of ions, Na^+ and Cl^-, from NaCl is ~ 2 eV. Calculate the approximate number of Schottky imperfections present in the NaCl crystal at room temperature.
4. The density of Schottky defects in a certain sample of sodium chloride is 5×10^{11} m^{-3} at 300 K. If the interionic separation is 2.82Å, what is the average energy required to create one Schottky defects?
5. The average energy required to create a Frenkel defect in an ionic crystal, $A^{2+}B^{2-}$, is 1.4 eV. Calculate the ratio of Frenkel defects at 300 K and 600 K in 1g of crystal.

ANSWER KEY

1. (6.185×10^{-26}, 9.084×10^{-6}) **2. (10^{-7}m, 1:10^3)** **3. (0.35×10^6 cm^{-3})**

4. (1.98 eV) **5. (1.316×10^{-6})**